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RESEARCHES ON THE DOUBLE HALIDES.

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In an article[1] published about two years ago I reviewed the evidence as to the nature and structure of the double halides. Attention was called:

(1) To the large number of the substances known as double halides.

(2) To the simplicity of the law governing the composition of these compounds.

(3) To the analogy of these compounds to the oxy-salts.

(4) To the arguments that lead to the conclusion that there are in general two classes of halides, which are to be regarded as basic and acidic, and which bear to each other relations like those that basic oxides bear to acidic oxides.

(5) To the arguments which appear to me fully to justify the conclusion that in the double halides we have a double halogen atom playing the same rôle that the linking oxygen plays in oxy-salts.

I have reason to believe that the views expressed in the article referred to have met with the approval of many. On the other hand, I am aware that there are some who are not willing to accept these views. The only arguments, however, that, so far as I know, have been put forward in opposition, are those contained in Professor Ramsay's recent book "A System of In-

[1] This Journal **11**, 291.

organic Chemistry,"[1] and a brief comment[2] by W. Ostwald in connection with an abstract of my article. The latter deserves mention in this place for the reason that the writer of the abstract has evidently overlooked an essential statement of my article. He calls attention to the fact that potassium ferrocyanide, $K_4Fe(CN)_6$, or $Fe(CN)_2.4KCN$, is an exception to the law of composition of the double halides pointed out by me. To this it need only be remarked that nitrogen compounds, at least the double halides containing ammonium, were distinctly excepted by me. On this point I here quote my own words: "The examples given in the above tables are fair representatives of the whole class of double halides, except that all ammonium compounds are omitted. The double halides formed with halogen salts of ammonium are very numerous, and many of them are quite complicated. There are indeed ammonium salts known belonging to all the classes above mentioned, but there are many others which do not belong to these classes. Considering the power of ammonium salts in general to form complex compounds with metallic salts, one cannot avoid the conclusion that there is some power in nitrogen which makes the formation of these compounds possible. The position of the double halides containing ammonium is certainly exceptional. They seem to be governed by some law of their own." Similarly, while there is, of course, a general analogy between cyanides and halides, it is not surprising that they do not conduct themselves exactly alike in all respects. It should be added, however, that there are a few double halides that correspond in composition to potassium ferrocyanide. These will be discussed further on.

Ramsay advances three arguments in opposition. These are given below, with a few comments suggested by them:

1. The figures obtained in the determination of the specific gravity of the vapors of aluminium methyl and of aluminium ethyl indicate that at lower temperatures these compounds must be represented by the formulas $Al_2(CH_3)_6$ and $Al_2(C_2H_5)_6$, while, at higher temperatures, they are plainly simpler and probably correspond to the formulas $Al(CH_3)_3$ and $Al(C_2H_5)_3$. This suggests that these compounds are like aluminium chloride which, at lower temperatures, gives figures leading to the formula Al_2Cl_6, while, at higher temperatures, the figures lead to the formula $AlCl_3$. From

[1] London: I. & A. Churchill, 1891. [2] Ztschr. physik. Chem. 4, 270.

these facts it appears that the compound Al_2Cl_6 cannot be explained by assuming that the two molecules $AlCl_3$ are held together by the chlorine atoms, for this same explanation cannot be applied to the case of methyl and ethyl compounds, as they contain no chlorine nor other halogen atoms. Further, as the existence of the complex molecule, Al_2Cl_6, cannot be explained in this way, it follows that the double halides cannot be explained in this way.

This argument cannot be regarded as a strong one, even assuming that the experimental basis is sufficient to justify the premises. It is by no means certain that aluminic chloride at lower temperatures is similar to the double halides. It seems to me probable that it is so, but there are some reasons for thinking that it may not be. The most prominent of these is the fact that the double halides seem to be formed by virtue of a certain oppositeness of character of the uniting halides, just as oxy-salts are formed in consequence, as we say, of the basic and acidic properties of the uniting oxides. In the double compound Al_2Cl_6 we have two molecules of the same kind united. What is the incentive to union in this case? Whatever it may be, it would seem at first sight to be different from that which leads to the formation of the double halides proper. Among oxygen compounds there are cases similar to aluminium chloride, as, for example, arsenious oxide, the specific gravity of whose vapor leads to the formula As_4O_6. No satisfactory explanation of these facts can be offered at present, though it seems to me probable that such compounds are analogous to ordinary salts. We do not hesitate to assume that the oxides Sb_2O_4, Fe_2O_4, Pb_2O_4, etc., are analogous to salts. If this assumption be true, it does not appear that we are violating any fundamental principle of chemistry in assuming that arsenious oxide is of the same order. So also the assumption that aluminium chloride, Al_2Cl_6, is analogous to the double chlorides is not without reason. The question then remains, is this doubled molecule analogous to the methyl and ethyl compounds of aluminium? Professor Ramsay says it is, but Quincke, the latest and by far the most careful experimenter on the organic derivatives of aluminium, thinks not. In an article[1] giving the results of his experiments he uses these words: "Diese Versuche nach dem Gasverdrängungsverfahren geben also keine Bestätigung der Resultate von Louïse und Roux; sie sprechen vielmehr in entschiedener Weise gegen

[1] Ztschr. physik. Chem. **3**, 165.

jede Existenz von Gasmolekülen der Form $Al_2(CH_3)_6$. Denn da bereits 10° oberhalb des Siedepunktes die Dichte um 20 per cent. kleiner ist, als der Formel $Al_2(CH_3)_6$ entspricht, so bestehen unzweifelhaft unter den obwaltenden Bedingungen Moleküle von dieser Grösse nicht. Demnach kann die Formel des Aluminiummethyls nur durch $Al(CH_3)_3$ ausgedrückt werden."

2. Ramsay's second argument is this: "It is impossible to class compounds containing water of crystallisation otherwise than as additive compounds, and there appears no reason to believe that double halides are otherwise constituted" (p. 506). This is simply begging the question. There was a time not long past when to call a substance a "molecular compound" was held to be an explanation. The farther the study of compounds is pushed the less room does there seem to be for molecular or additive compounds. As for myself, I am not prepared to deny the existence of additive compounds as something different from substitutive or atomic compounds, nor, I may add, am I prepared to admit their existence. It seems more probable that, when our knowledge of that property of atoms which we call valence—so important and yet so little understood—shall have been sufficiently extended, we shall see that the existence of all chemical compounds, whether molecular or atomic, is due to the operation of the same cause. This is, of course, worth nothing as an argument, but I think it is worth as much as the opinion expressed by Ramsay.

3. The third argument is this: If the supposition that the double halides are formed "by virtue of the halogen elements, which in such compounds function as *triads* towards each other, . . . it becomes possible to represent any double halides whatever constitutionally. . . . Given the hypothesis, all double halides may be thus represented by a little ingenuity." While the hypothesis referred to does admit the existence of many double halides, it certainly excludes many. It is not true that by means of it any double halides whatever can be represented constitutionally. For example, while the compounds KF.HF, KF.2HF, and KF.3HF, which are known, can be explained, the compound KF.4KF, which is not known, cannot be explained. As well find fault with the law of multiple proportions because it suggests an infinite number of possibilities, or with the valence hypothesis because it can be used to explain many things unknown to man.

There is evidently some law limiting the application of the law of multiple proportions, as there is some law limiting the valence of elements. We first recognise the general truth and then strive to learn what its limitations are.

Since the publication of my first article,[1] investigations have been carried on under my guidance for the purpose of testing the law of composition of the double halides deduced by me from a consideration of the facts. This law as first stated is as follows:

When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms contained in the latter.

This law is based on a study of the composition of between four and five hundred cases. Attention was called, however, to the existence of one exception to the law, viz., the salt $CuCl.2KCl$ or $Cu_2Cl_4.4KCl$. Further examinations of the literature have brought to light a few more exceptions, and the first object of the researches, an account of which follows, was to determine whether the anomalous salts could be obtained or not.

The double halides of tin were investigated by Mr. G. M. Richardson for the purpose of determining whether the salt $SnCl_2.4KCl.3H_2O$, which has been described by Poggiale,[2] exists. It having been found impossible to make this salt, the investigation was pushed in various directions. A number of other double halides of tin were examined, and the work shows that all the salts thus far made conform to the above law.

The double halides of lead were investigated by Mr. C. H. Herty. Several double iodides of lead have been described, and among them one having the composition $K_4PbI_6(PbI_2.4KI)$. This was described by Boullay.[3] Mr. Herty's work proves that this salt cannot be obtained, and, furthermore, that the only double iodide of lead that can be obtained under ordinary conditions is the one having the composition $KPbI_3.2H_2O$ ($PbI_2.KI.2H_2O$). This is the only double iodide obtained by us, though the conditions were modified in every way that the imagination suggested. The investigation showed further that there is a well crystallised salt of the formula $KPbBr_3.H_2O$, and another of the formula $KPbCl_3$. So far as has been determined, then, up to the present, the double halides of lead conform to the law.

[1] Loc. cit. [2] Pogg. Ann. **94**, 507. [3] Ann. chim. phys. [2] **34**, 366.

The study of the double halides of manganese and of some of those of antimony was carried out by Mr. C. E. Saunders. As regards the manganese compounds, they were found to conform to the law in every respect, and, as they were exhaustively studied, it may safely be asserted that there is no exceptional double halide of manganese. Among the antimony compounds there are, however, some very peculiar ones. They are not exceptions to the law, but it must be confessed that they put the hypothesis as to the structure of the double halides to a severe test. Godeffroy[1] has described two peculiar double chlorides of antimony, one containing cæsium and the other rubidium. To these he assigns the formulas $SbCl_3.6CsCl$ and $SbCl_3.6RbCl$. These plainly form marked exceptions to the law, and the results of their investigation were awaited with special interest. Mr. Saunders has shown that these salts have no existence. On the other hand, while the salts found are for the most part comparatively simple, two of them are specially noteworthy. The simpler salts are those represented by the formulas $Cs_2Sb_2Cl_9$, which is the only double chloride of cæsium and antimony, and $RbSbCl_4$. Those of peculiar composition are represented by the formulas $Rb_5Sb_5Cl_{14}$ and $Rb_{23}Sb_{10}Cl_{53}$, or, writing them in the usual way, these formulas are $3SbCl_3.5RbCl$ and $10SbCl_3.23RbCl$. The peculiarity of the composition of these salts led to special precautions in their analysis. The results obtained cannot be brought in harmony with simple formulas. The more complex of these salts is the one most easily obtained and most easily purified. It crystallises beautifully, and its properties are altogether such as to show that we were working with a pure substance. There seems therefore no escape from the conclusion that the salt has the above formula or one very near it. An attempt to express the structure of this salt by means of the hypothesis found so useful in all the other cases thus far discussed showed that the simple conception of a double chlorine atom acting as an oxygen atom is not sufficient, and that to account for this remarkable case it is necessary to assume that three chlorine atoms act together in such a way so as to form a trivalent group. If this salt were the only one necessitating this assumption the suggestion would not be justifiable, but there are a few well-established simple cases which can be accounted for only in this way. There are, for example, the salts $CuCl.2KCl$ and

[1] Zeitschr. des allg. österr. Apotheker-Vereins, 1874, 161, and Ber. d. chem. Gesell. 7, 375.

$CdCl_2.4KCl$. The former was first described by Mitscherlich,[1] and a recent examination of the salt by Mr. Richardson in this laboratory has shown that it undoubtedly exists. The latter was described by Von Hauer,[2] and Mr. Richardson has also examined this with the same results. While nearly all double halides conform to the law and are therefore in accordance with the hypothesis of the double halogen atom acting as a bivalent group, there are a few—*not more than three or four out of over four hundred*—that cannot be explained in this way. In these exceptional cases it seems necessary to assume that three halogen atoms acting together form a trivalent group $>(Cl_2)—$, or, assuming that chlorine is trivalent, the group must be represented structurally thus: $—Cl\begin{matrix}/Cl— \\ | \\ \backslash Cl—\end{matrix}$. I am aware that such considerations will not be likely to meet with approval, but let the fact be again emphasised that most double halides have a simple composition, in nearly all cases showing analogy with the corresponding oxygen compounds; that there is nothing indefinite in their composition; that the law governing the composition of nearly all of them is certainly very simple. Let any one carefully study the facts and he will without doubt reach the conviction that in the double halides we have to deal not with the results of the haphazard combination of molecules, but with compounds as definite as any known to us. It cannot be that they should be classed apart.

Mr. C. P. Brigham has studied some of the double halides of bismuth, the investigation having been undertaken principally with the object of determining whether the two salts described by Godeffroy, Rb_6BiCl_9 ($BiCl_3.6RbCl$), and Cs_6BiCl_9 ($BiCl_3.6CsCl$), exist or not. As was expected after the results of the work of Mr. Saunders, these salts cannot be obtained. Bismuth chloride forms, however, three salts with rubidium chloride. These have the following formulas: $RbBiCl_4.H_2O$ ($BiCl_3.RbCl.H_2O$), Rb_3BiCl_6 ($BiCl_3.3RbCl$), and $Rb_{23}Bi_{10}Cl_{53}$ ($10BiCl_3.23RbCl$). The last one has, as will be seen, the same complicated composition as the rubidium salt of antimony chloride already referred to. With cæsium chloride, bismuth chloride forms two salts with the following formulas: Cs_3BiCl_6 ($BiCl_3.3CsCl$), and $Cs_3Bi_2Cl_9$ ($2BiCl_3.3CsCl$). All the above salts conform to the law. Mr. Brigham has also

[1] Ann. chim. phys. **73** (1840), 384. [2] Jour. prak. Chem. **64**, 486.

studied a few other double halides of bismuth. On comparing the formulas of the salts containing sodium, potassium, rubidium, and cæsium, a curious and interesting regularity as regards the water of crystallisation is observed. The formulas of the salts are here given: $Na_3BiCl_6.3H_2O$, $K_2BiCl_5.2H_2O$, $RbBiCl_4.H_2O$, and Cs_3BiCl_6. As the atomic weight of the metallic element increases, the number of molecules of water of crystallisation decreases. A similar regularity is observed on comparing the formulas of some of the salts described by Mr. Herty. In the series $KPbI_3.2H_2O$, $KPbBr_3.H_2O$, and $KPbCl_3$, there is a regular decrease in the number of molecules of water of crystallisation. In this series the variable is the halogen, and the amount of water of crystallisation decreases as the atomic weight of the halogen decreases.

If the specific gravity of some double halide in the form of vapor could be determined, and the results should be found to accord with those required by the commonly accepted formula, that one at least would be rescued from the slough of "molecular compounds." Accordingly, some efforts have been made to secure such determinations. Landolph[1] states that, when anethol is treated with boron trifluoride, a compound of the formula HBF_4 is formed, and he describes this as boiling at 130° with partial decomposition. Indeed, the author gives the results of the determination of the specific gravity of its vapor, and these results are well in accord with the theory. It is needless to point out the importance of this observation for the whole subject of double halides. Unfortunately, the observation could not be verified. Mr. R. de Roode undertook the repetition of this work. He followed the directions with the greatest care and repeated the experiment a number of times, but only with negative results as far as the main point is concerned. Nothing could be obtained corresponding in properties to the compound described, and we were reluctantly compelled to give up the work, with the conviction that no aid can be obtained from that source.

Again, a compound of sulphur chloride and mercurous chloride has been described by Capitaine.[2] He gave it the formula $SCl_2.Hg_2Cl_2$, and stated that it could be vaporised without decomposition. Mr. J. E. Gilpin has undertaken the preparation and

[1] C. R. **86**, 603.

[2] Journ. de Pharmac. **25**, 566; and Journ. prak. Chem. **18**, 437.

study of this compound. He has found that there is no difficulty in preparing it in any desired quantity; that it is a well crystallised compound of definite composition with the above formula. He has further shown that, as stated by Capitaine, when heated it is converted into vapor and again deposited, apparently unchanged. Careful study has proved, however, that it suffers dissociation under the influence of heat, its constituents recombining when the temperature is lowered. As determinations of the specific gravity of the vapor of a substance conducting itself in this way would be of no value, the determinations were not made.

I hope in the near future to make determinations of the specific gravity of the vapor of the double chloride of aluminium and sodium at different temperatures. Whether such determinations are feasible remains to be seen. From the published accounts of the compound, I judge that work in this line is promising. Deville states[1] that it can be converted into vapor without decomposition. I shall also continue my efforts with other compounds, both with reference to their composition and to the specific gravity of their vapors. The peculiar results obtained in the study of the rubidium salts of antimony and of bismuth chlorides furnish an incentive to the study of other double halides containing rubidium, and such work will be undertaken here. Mr. H. C. Jones is at present engaged in the study of the double halides of gold, and, in the course of this investigation, we propose to examine the salts containing rubidium.

The detailed accounts of the investigations referred to in this general account are given below.

I.—On the Double Halides of Tin.[2]

By George M. Richardson.

Compounds of Stannous Chloride and Potassium Chloride.

Poggiale[3] has described a salt of the formula $SnCl_2.4KCl.3H_2O$. In addition to this salt, one of the composition $SnCl_2.2KCl$ is recorded, but there seems to be some confusion regarding it.

[1] Ann. ch. phys. [3], **43**, 25.

[2] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1890.

[3] Pogg. Ann. **94**, 507.

Graham gives it the formula $SnCl_2.2KCl.3H_2O$: Mitscherlich in his text-book speaks of the salt $SnCl_2.2KCl.2H_2O$; Apjohn describes the salt $SnCl_2.2KCl.H_2O$ and states that it crystallises in octahedra. Rammelsberg has analysed[1] and measured[2] an orthorhombic salt to which he assigns the formula $SnCl_2.2KCl.H_2O$, and says further that the octahedra obtained by Apjohn were probably the stannic salt $SnCl_4.2KCl$. This salt is frequently formed along with stannous salt. Marignac[3] confirmed the results of Rammelsberg.

The double halides here described were prepared, in most cases, by mixing the solutions of the constituent halides. The alkaline halide was dissolved in water, and the tin solution was made by dissolving tin in hydrochloric acid or hydrobromic acid, an excess of tin being present to prevent the presence of free acid in the solution.

Mono-potassium chloro-stannite, $KSnCl_3.H_2O$.—When a solution of potassium chloride is mixed with a solution of stannous chloride in such proportions that the stannous chloride is present in large excess, white, hair-like crystals will form after a time, or, if the solutions are nearly saturated, at once. These crystals, carefully dried by pressing between drying papers, were analysed with the following results:

	Found.	Calculated.
Sn	41.60 per cent.	41.91 per cent.
K	14.09	13.88
Cl	38.15	37.82
H_2O	5.88	6.39
	99.72	100.00

From which it appears that the formula is $SnCl_3KCl.H_2O$ or $KSnCl_3.H_2O$.

This salt is quite stable in the air; it does not lose its water of crystallisation over sulphuric acid, but loses it at 100°, without suffering further change. Heated to high temperatures it loses hydrochloric acid with its water of crystallisation, and is thus decomposed, oxides of tin being formed. The salt is decomposed by water, forming a turbid solution; it dissolves, forming a clear solution, in hot hydrochloric acid or in a hot solution of potassium chloride, but from both of these solutions there crystallises out

[1] Pogg. Ann. **94**, 507. [2] Krystal. Chemie, p. 211. [3] Jahresber. 1857, 221.

on cooling a salt having the composition $SnCl_4.2KCl.2H_2O$ or $K_2SnCl_4.2H_2O$.

Di-potassium chloro-stannite, $K_2SnCl_4.2H_2O$.—If, instead of having the stannous chloride present in large excess, the solutions are mixed in about equal portions or the potassium chloride is present in excess, large, opaque, white, orthorhombic crystals are formed after standing for a time. The crystals, carefully dried and analysed, gave the following results:

	Found.		Calculated.
	A.	B.	
Sn	31.54 per cent.	31.46 per cent.	31.55 per cent.
K	20.64	21.48	20.86
Cl	38.54	37.59	37.97
H_2O	9.37	10.47	9.62
	100.09	101.00	100.00

These results show that the formula is $K_2SnCl_4.2H_2O$. This salt is perfectly stable in the air. A sample which had been exposed to the action of the atmosphere for forty days gave with ferric chloride and standard permanganate solution 31.49 per cent. of stannous tin, the theory being 31.55 per cent. It does not lose its water of crystallisation over sulphuric acid, but gradually loses the whole of it at 100° without change. It can be recrystallised without change from hydrochloric acid, being quite soluble in the hot acid and comparatively insoluble in the cold acid. It can also be recrystallised from a potassium chloride solution without change of composition. The habit of the crystals formed in the two cases is quite different; from the hydrochloric acid they are much elongated, parallel to the C axis, and rarely have terminal planes, while from the potassium chloride solution they are less elongated and the terminal planes are well formed.

Di-potassium chloro-stannite, $K_2SnCl_4.H_2O$.—When large quantities of the salt just described, $K_2SnCl_4.2H_2O$, are dissolved in hot hydrochloric acid and the solution quickly cooled, a white crystalline precipitate is formed, and after a few moments crystals of the salt $K_2SnCl_4.2H_2O$ begin to grow, and increase in size with great rapidity. If the crystalline precipitate is removed before the crystals of the second salt begin to form, and is analysed, it is found to have the formula $K_2SnCl_4.H_2O$, that is, it differs by one molecule of water of crystallisation from the large crystals.

The following results were obtained by analysis:

	Found.	Calculated.
Sn	33.05 per cent.	33.15 per cent.
K	21.48	21.91
Cl	39.11	39.89
H_2O	...	5.05
		100.00

This salt also is stable in the air, but if left in its mother-liquor it gradually takes up more water of crystallisation and is transformed into the salt $K_2SnCl_4.2H_2O$. It does not lose its water of crystallisation over sulphuric acid, but loses it at 100°. If this salt or the one with two molecules of water be dissolved in hot stannous chloride solution, the salt $KSnCl_3.H_2O$, already described, crystallises out on cooling.

All efforts to prepare other salts composed of stannous chloride and potassium chloride than those just described have proved fruitless. The salt $K_2SnCl_4.2H_2O$ was dissolved in potassium chloride solution in the hope of getting the salt described by Poggiale, but in vain; the salt $K_2SnCl_4.2H_2O$ was again obtained and the excess of potassium chloride crystallised out by itself.

The solutions were mixed so that a large excess of potassium chloride was present, but with the same result, the potassium chloride in excess of that required for the salt $K_2SnCl_4.2H_2O$ crystallised out alone, for the most part in transparent octahedra.

The mother-liquors from these crystals were evaporated and a second and third crop of crystals obtained, but always with the same result. By the evaporation there were also formed octahedra of the well-known stannic salt K_2SnCl_6 or $SnCl_4.2KCl$, since the evaporation of the solutions oxidises the tin.

When a saturated solution of stannous chloride is added to a saturated solution of potassium chloride, crystals form very rapidly, and so completely fill the liquid in a few moments that it can be inverted without loss of the solution. An examination of this mass proves it to consist of all three of the salts above described, but upon standing a few days, if sufficient potassium chloride is present, it will be entirely converted into the salt $K_2SnCl_4.2H_2O$, otherwise there will remain a mixture of the two salts $K_2SnCl_4.2H_2O$ and $KSnCl_3.H_2O$; the latter salt appears to

be stable only in the presence of a considerable excess of stannous chloride if allowed to remain in the solution from which it has crystallised. So also, as we have seen, the salt $K_2SnCl_4.H_2O$ will take up an additional molecule of water if it be allowed to stand in its mother-liquor for several days; but if it be removed before long standing it is possible to get a mass of crystals of $K_2SnCl_4.2H_2O$, which are in a matrix of the salt $K_2SnCl_4.H_2O$.

Compounds of Stannous Chloride and Ammonium Chloride.

Mono-ammonium chloro-stannite, $NH_4SnCl_3.H_2O$.—This salt is prepared just as the corresponding potassium salt and, as far as determined, it is analogous to the potassium salt in every respect, with the exception that the tendency to pass over into the orthorhombic form is here even more marked than in the case of the potassium salt.

Di-ammonium chloro-stannite, $(NH_4)_2SnCl_4.2H_2O$.—This salt is very readily obtained by bringing the solutions of the component chlorides together and allowing them to stand. It is isomorphous with the corresponding potassium salt, which it resembles in its general properties. The tin and water were determined in this salt with the following results:

	Found.	Calculated.
Sn	35.54 per cent.	35.58 per cent.
H_2O	9.95	10.84

This analysis proves its formula to be $(NH_4)_2SnCl_4.2H_2O$.

All efforts to prepare the salt with one molecule of water of crystallisation, $(NH_4)_2SnCl_4.H_2O$, analogous to the potassium salt $K_2SnCl_4.H_2O$, have been unsuccessful.

Crystals of the salt $(NH_4)_2SnCl_4.2H_2O$ and of the salt $K_2SnCl_4.2H_2O$ have been measured[1] and they are found to be the same as those measured by Rammelsberg,[2] yet he ascribes to them the composition represented by the formulæ $(NH_4)_2SnCl_4.H_2O$ and $K_2SnCl_4.H_2O$. For the potassium salt he gives the following analysis:[3]

[1] See crystallographic measurements, pages 101–103 of this paper.
[2] In his Krystal. Chemie, 211 and 212.
[3] Pogg. Ann. **94**, 510.

	Found. A.	Found. B.	Calculated.
K	23.07 per cent.	22.79 per cent.	22.00 per cent.
Sn	33.32	33.58	33.07
Cl	...	...	39.87
H_2O	...	...	5.06

From these results it would appear that Rammelsberg had measured one salt and analysed another. This is not improbable, since they may both occur in the same crystal mass.

But how is it with regard to the ammonium salt? We have seen that the ammonium salt with one molecule of water of crystallisation cannot be prepared, so that it would be impossible to make a similar mistake here.

He obtained by analysing his ammonium salt the following results:[1]

	Found.	Calculated.
NH_4	10.24 per cent.	11.49 per cent.
Sn	35.93	37.52
Cl	44.39	45.25
H_2O	...	5.74

On the basis of this analysis he assigned to the salt the formula $(NH_4)_2SnCl_4.H_2O$. But the calculated results for the formula with two molecules of water are:

NH_4	10.84 per cent.
Sn	35.54
Cl	42.78
H_2O	10.84
	100.00

These calculated results agree more closely with Rammelsberg's analysis than do the results calculated from the formula which he assigns to the salt, so that his own analysis proves that the formula for the ammonium compound at least is $(NH_4)_2SnCl_4.2H_2O$ and not $(NH_4)_2SnCl_4.H_2O$.

Poggiale in describing the salts $SnCl_2.4KCl.3H_2O$ and $SnCl_2.4NH_4Cl.3H_2O$ gives no analyses, but says that the salts were obtained directly from a mixture of the solutions in beautiful long needles. The salts he obtained were in all probability K_2SnCl_4.

[1] Loc. cit.

$2H_2O$ and $(NH_4)_2SnCl_4.2H_2O$, or as they are usually written $SnCl_2.2KCl.2H_2O$ and $SnCl_2.2NH_4Cl.2H_2O$.

The Action of Stannous Chloride upon Sodium Chloride and Lithium Chloride.—If saturated solutions of stannous chloride and sodium chloride be mixed no crystals are formed. If the solution be evaporated or allowed to stand over sulphuric acid for a long time the solution becomes thick and oily, and finally after the volume of the liquid has been much reduced sodium chloride crystallises out alone.

Lithium chloride behaves in the same way.

Compounds of Stannous Bromide and Potassium Bromide.

Very little is said of these compounds in the literature. They are spoken of only in connection with the chlorides, and are said to be similar to them.

Mono-potassium bromo-stannite, $KSnBr_3.H_2O$.—On adding a solution of potassium bromide to a solution of stannous bromide, bundles of long hair-like crystals are formed almost instantly, if the solutions are concentrated, and these grow with great rapidity until the vessel is quite filled with them. These crystals were analysed with the following results:

	Found.	Calculated.
Sn	27.77 per cent.	28.43 per cent.
H_2O	4.35	4.34

This salt is similar in appearance to the corresponding chloride, and like it is quite stable in the air, retains its water of crystallisation over sulphuric acid, but loses it at 100° without change of the salt. But it differs from the chloride in being much more readily formed from the mixed solutions, being formed even in the presence of an excess of potassium bromide. It can be recrystallised from hydrobromic acid, and even from a solution of potassium bromide.

Di-potassium bromo-stannite, $K_2SnBr_4.2H_2O$.—As just seen, when solutions of stannous bromide and potassium bromide are mixed the salt $KSnBr_3.H_2O$ is always formed, but if there is present an excess of potassium bromide, or if the salt $KSnBr_3.H_2O$ is dissolved in a solution of potassium bromide, and the crystals which separate out on cooling are allowed to stand several days in the solution, it will be found that large orthorhombic crystals are scattered through the mass of other crystals.

This salt is similar to the corresponding chloride in its general appearance and in its properties. An analysis of the crystals led to the results that follow, proving its formula to be $K_2SnBr_4.2H_2O$.

	Found.	Calculated.
Sn	21.08 per cent.	21.38 per cent.
H_2O	6.12	6.52

The salt cannot be recrystallised from its solutions in hydrobromic acid; if it is dissolved in this acid the salt $KSnBr_3.H_2O$ crystallises out. A salt with one molecule of water of crystallisation analogous to the chloride $K_2SnCl_4.H_2O$ was not obtained.

Compounds of Stannous Bromide and Ammonium Bromide.

Mono-ammonium bromo-stannite, $NH_4SnBr_3.H_2O$.—On mixing the solutions of stannous bromide and ammonium bromide hair-like crystals of $NH_4SnBr_3.H_2O$ are at once formed. In its general properties this salt is like other analogous salts already described; it differs from the corresponding chloride, $NH_4SnCl_3.H_2O$, in that it is much more readily formed from the mixed solutions, and it differs from the corresponding potassium salt, $KSnBr_3.H_2O$, in being less readily formed from the mixed solutions, and in passing more readily over into the orthorhombic variety.

Di-ammonium bromo-stannite, $(NH_4)_2SnBr_4.2H_2O$.—Crystals of this salt are obtained by mixing the two solutions so that ammonium bromide is present in excess, and allowing the salt $NH_4SnBr_3.H_2O$, which is at first formed, to stand. It resembles the other corresponding salts already described. Analyses of the crystals gave:

	Found.		Calculated.
	A.	B.	
Sn	23.00 per cent.	22.97 per cent.	23.14 per cent.
H_2O	6.34		7.06

Crystals of this salt are more readily obtained than the crystals of the salt $K_2SnBr_4.2H_2O$, but are not so easily obtained as either of the chlorides $K_2SnCl_4.2H_2O$ or $(NH_4)_2SnCl_4.2H_2O$.

Compounds containing Chlorine and Bromine.

Compounds of Stannous Bromide with Potassium Chloride.—When a solution of potassium chloride is added to a solution of stannous bromide, hair-like crystals are formed, just as when the two chlorides or the two bromides are mixed, and it was thought from the analogy that the salt $KSnBr_3Cl.H_2O$ or $SnBr_2KCl.H_2O$

was formed, but on analysis it was found not to yield constant results. Several specimens of this salt were prepared, and the tin was determined with the following results:

Sample A gave 28.63 per cent. Sn.
" B " 29.66
" C " 31.19
" D " 30.04
" E " 29.21.

The calculated percentage of tin in a salt having the formula $SnBr_2KCl.H_2O$ is 31.84 per cent. Possibly different salts are formed as follows:

$$4SnBr_2 + 4KCl + 4H_2O = \begin{cases} SnBr_2KBrH_2O & (1) \\ 2)SnBr_2KClH_2O & (2). \\ SnCl_2KBrH_2O & (3) \end{cases}$$

The calculated amounts of tin in these salts are, (1) 28.43 per cent.; (2) 31.84 per cent.; (3) 36.18 per cent.

Or, more probably, it is a mixture of the two salts $KSnBr_3.H_2O$ and $KSnCl_3.H_2O$, the former being present in excess, as we should expect, since we have seen that it is much more readily formed than the latter. The percentage of tin in these two salts is:

$KSnBr_3.H_2O = 28.43$
$KSnCl_3.H_2O = 41.91.$

In order to decide this point, further investigation is necessary.

A similar mixture is obtained when potassium bromide solution is added to stannous chloride solution. The same is true of solutions of ammonium chloride and stannous bromide, or of ammonium bromide and stannous chloride. When the alkaline halide is added in excess, orthorhombic crystals are formed.

An analysis of some of the crystals formed by adding potassium chloride to stannous bromide led to the formula $K_2SnCl_2Br_2.2H_2O$. The results of the two analyses are as follows:

	Found. A.	Found. B.	Calculated.
Sn	25.63 per cent.	25.48 per cent.	25.49 per cent.
K	17.21	17.17	16.85
Br	36.60	36.70	34.56
Cl	15 46	14.94	15.33
H_2O	4.60	...	7.77
	99.50		100.00

Similar crystals were made by mixing the solutions of stannous chloride and potassium bromide, and these were analysed with the following results:

	Found.
Sn	24.18 per cent.
K	16.66
Br	34.43
Cl	15.27
H_2O	8.01
	98.55

which leads to the same formula, $K_2SnCl_2Br_2.2H_2O$, as assigned to the crystals prepared from stannous bromide and potassium chloride. These crystals could not be distinguished from one another in any way.

These crystals, when heated in a current of dry air, first lose water with some hydrochloric acid and some hydrobromic acid, with the formation of oxychloride and oxybromide of tin; then stannous chloride and stannous bromide sublime and are deposited in the cooler parts of the tube, leaving behind a mixture of potassium chloride, potassium bromide, tin oxychloride, and tin oxybromide. If the water be first driven off at 100° and the dried salt heated in a current of dry hydrogen, the stannous bromide and chloride sublime, leaving potassium bromide and chloride behind. There is also a slight reduction of the tin to the metallic state, and both hydrochloric and hydrobromic acids are given off.

The angles of these two series of crystals appear to be the same, but the faces gave such poor reflections and so many images that accurate measurements could not be made. With the hope of getting better crystals, several more specimens of the salt were prepared from solutions of different strengths. Upon analysis these new specimens were found to contain varying amounts of tin. Six specimens gave respectively 25.04, 25.71, 26.02, 26.59, 27.34, and 26.94 per cent. of tin.

The faces of these crystals also gave poor reflections and multiple images, yet a variation in angle could be detected in the crystals of different composition.

In the case of the ammonium salt the reflections are much better and the crystals can be very accurately measured. The crystals from different solutions are found to vary in their angles,

and upon analysis are found to be of variable composition. A determination of tin in four different specimens resulted as follows: 24.29, 24.42, 25.20, and 25.56 per cent. of tin.

The calculated amount of tin in a compound having the formula $(NH_4)_2SnBr_2Cl_2.2H_2O$ is 28.03 per cent. These results suggest that we have here to deal with an isomorphous mixture of the chloride and the bromide. If this be the case it ought to be possible to get crystals varying in their percentage of tin from 21.38 per cent. in the case of the pure salt $K_2SnBr_4.2H_2O$ to 31.55 per cent. in the case of the pure salt $K_2SnCl_4.2H_2O$, and from 23.14 per cent. to 35.55 per cent. in the case of the ammonium salts. A further study of these salts will be carried out in order to determine the amount of change in angle measurement that accompanies a given change in composition, and to decide, if possible, whether or not the molecule $K_2SnCl_2Br_2.2H_2O$ exists.

R. W. Atkinson[1] has prepared the salt $K_2SbCl_3Br_2.1\frac{1}{2}H_2O$ by mixing antimony chloride and potassium bromide, and the same salt by mixing potassium chloride with antimony bromide. And R. H. Solly[2] has proved their crystallographic identity. Atkinson also obtained crystals to which he gives the formula $Sb_2Cl_6Br_2K_2.2H_2O$ and $SbCl_3BrK.H_2O$; he does not speak of having any difficulty in obtaining pure specimens.

Summary of the Results.

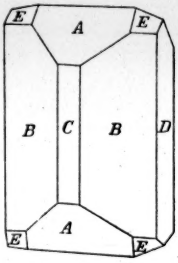
It is clear, then, that stannous chloride and bromide form two classes of salts with potassium and ammonium bromide and chloride. One class contains one molecule of the alkaline halide, and the other class contains two molecules of the alkaline halide. In the case of the chlorides the tendency to form the salt with two molecules of the alkaline chloride is very strong, and is even more marked with the ammonium chloride than with the potassium chloride. With the bromides on the other hand the tendency is to form the salt with one molecule of the alkaline bromide, while the one with two molecules of the alkaline bromide is obtained with greater difficulty, and here too the salt with two molecules of ammonium bromide is much more readily obtained than the potassium salt.

The salts of lithium and sodium, if formed at all, are so soluble that they cannot be crystallised.

[1] Jour. Chem. Soc. 43 (1883), 289. [2] Ibid. 293.

Crystallographic Examination of Salts.

We have seen that the salts $K_2SnCl_4.2H_2O$, $(NH_4)_2SnCl_4.2H_2O$, $(NH_4)_2SnBr_4.2H_2O$, $K_2SnBr_4.2H_2O$ are all orthorhombic in their crystallisation and that they have the same habit, the most general form being that shown in the figure, in which



$A = P\overline{\infty}$
$B = \infty P$
$C = \infty P\overline{\infty}$
$D = \infty P\breve{\infty}$
$E = P$

Most of the crystals consist simply of the two forms ∞P and $P\overline{\infty}$, others are modified by $\infty P\overline{\infty}$ and $\infty P\breve{\infty}$ and rarely P. The salt $K_2SnBr_4.2H_2O$, however, rarely has the $P\overline{\infty}$ developed, but is terminated by P instead.

In the following observations the faces of the crystals are classified as *poor* (p), *fair* (f), *good* (g), *very good* (v. g.) according to the clearness of the reflected image which they give. In making up the means of the observations the different observations were given different weight according to the perfectness of the reflected image.

The following weights were assigned to the different observations:

2 poor images have a weight of 1.
1 poor image and 1 fair image have a weight of 2.
1 poor image and 1 good image have a weight of 3.
1 poor image and 1 very good image have a weight of 4.
2 fair images have a weight of 5.
1 fair image and 1 good image have a weight of 6.
1 fair image and 1 very good image have a weight of 7.
2 good images have a weight of 8.
1 good image and 1 very good image have a weight of 9.
2 very good images have a weight of 10.

The means where each observation has the same weight are also calculated for comparison.

But for calculation of the axial ratios the numbers obtained by the use of weights were taken in every case.

Measurements of Di-potassium Chloro-stannite, $K_2SnCl_4.2H_2O$.

Obtuse prism angle, B to B over C.

Crystal measured.	Weight of observation.	Observed angle.	Calculated angle and differences.
			111° 9′ 35″
No. 2, 2 f.	5	111° 13′ 30″	+ 3 55
No. 3, 2 v. g.	10	111 10 30	+ 0 55
No. 4, 2 f.	5	111 11 00	+ 1 25
No. 8, 2 f.	5	111 6 30	— 3 05
No. 11, 1 v. g. and 1 g.	9	111 7 30	— 2 05
Mean,		111 9 48	+ 0 13
Mean with weights,		111 9 36	+ 0 01

Acute prism angle, B to B over D.

			68° 50′ 25″
No. 3, 1 v. g. and 1 g.	9	68° 49′ 00″	— 1 25
No. 5, 1 g. and 1 f.	6	68 51 00	+ 0 35
No. 6, 2 g.	8	68 49 30	— 0 55
No. 8, 2 f.	5	68 51 30	+ 1 05
No. 9, 2 g.	8	68 51 00	+ 0 35
No. 11, 2 v. g.	10	68 51 00	+ 0 35
Mean,		68 50 30	+ 0 05
Mean with weights,		68 50 25	0 00

Angle of macrodome, A to A over top.

			84° 10′ 46″
No. 6, 1 v. g. and 1 f.	7	84° 12′ 00″	+ 1 14
No. 7, 1 g. and 1 p.	3	84 6 00	— 4 46
No. 8, 1 v. g. and 1 f.	7	84 11 00	+ 0 14
No. 9, 1 v. g. and 1 g.	9	84 10 30	— 0 16
No. 11, 2 g.	8	84 11 30	+ 0 44
Mean,		84 10 12	— 0 34
Mean with weights,		84 10 46	0 00

Angle from prism to macropinacoid, B to C.

			145° 34′ 48″
No. 2, 2 g.	8	145° 37′ 30″	+ 2 42
No. 3, 1 v. g. and 1 g.	9	145 35 30	+ 0 42
No. 5, 2 p.	1	145 29 00	— 5 48
No. 9, 1 f. and 1 p.	2	145 37 00	+ 2 12
No. 11, 1 v. g. and 1 p.	4	145 36 00	+ 1 12
Mean,		145 35 00	+ 0 12
Mean with weights,		145 36 06	+ 1 18

Angle from prism to brachypinacoid, B to D

			124° 25′ 12″
No. 3, 1 v. g. and 1 g.	9	124° 24′ 30″	— 0 42
No. 4, 1 f. and 1 p.	2	124 28 00	+ 2 48
No. 6, 1 v. g. and 1 g.	9	124 23 30	— 1 42
No. 8, 2 f.	5	124 25 00	— 0 12
No. 9, 2 g.	8	124 24 00	— 1 12
No. 11, 1 v. g. and 1 g.	9	124 25 30	+ 0 18
Mean,		124 25 05	— 0 07
Mean with weights,		124 24 38	— 0 34

Angle from prism to macrodome, B to A.

			127° 44′ 47″
No. 3, 2 v. g.	10	127° 46′ 00″	+ 1 13
No. 4, 1 f. and 1 p.	2	127 43 30	— 1 17
No. 6, 1 g. and 1 f.	6	127 43 30	— 1 17
No. 8, 2 v. g.	10	127 43 00	— 1 47
No. 9, 2 f.	5	127 43 00	— 1 47
No. 11, 2 v. g.	10	127 44 30	— 0 17
Mean,		127 43 55	— 0 52
Mean with weights,		127 44 08	— 0 39

From the angles 68° 50′ 25″ and 84° 10′ 46″ the value of the axes may be calculated, and the axial ratio is found to be

a : b : c as 0.685231 : 1 : 0.758634.

Measurements of Di-ammonium Chloro-stannite, $(NH_4)_2SnCl_4.2H_2O$.

Obtuse prism angle, B to B over C.

			111° 39′ 30″
No. 15, 2 p.	1	111° 37′ 00″	— 2 30
No. 16, 2 p.	1	111 43 00	+ 3 30
No. 19, 2 p.	1	111 39 00	— 0 30
No. 20, 2 f.	5	111 39 00	— 0 30
No. 21, 1 v. g. and 1 f.	7	111 39 00	— 0 30
No. 20, 2 f.	5	111 40 30	+ 1 00
Mean,		111 39 35	+ 0 05
Mean with weights,		111 39 28	— 0 02

Acute prism angle, B to B over D.

			68° 20′ 30″
No. 13, 2 f.	5	68 21′ 30″	+ 1 00
No. 15, 2 f.	5	68 23 00	+ 2 30
No. 16, 2 p.	1	68 21 00	+ 0 30
No. 17, 2 p.	1	68 22 30	+ 2 00
No. 18, 2 p.	1	68 25 00	+ 4 30
No. 19, 2 f.	5	68 27 00	+ 6 30
No. 20, 2 f.	5	68 20 30	0 00
No. 21, 2 v. g.	10	68 16 00	— 4 30
Mean,		68 22 04	+ 1 34
Mean with weights,		68 20 27	— 0 03

Angle of macrodome, A to A over top.

			84° 7′ 43″
No. 13, 1 g. and 1 p.	3	84° 11′ 00″	+ 3 17
No. 15, 2 f.	5	84 11 00	+ 3 17
No. 16, 1 f. and 1 p.	2	84 05 00	— 2 43
No. 17, 1 g. and 1 p.	3	84 09 00	+ 1 17
No. 19, 2 f.	5	84 07 00	— 0 43
No. 20, 1 v. g. and 1 f.	7	84 07 00	— 0 43
No. 21, 2 f.	5	84 04 30	— 3 13
Mean,		84 07 47	+ 0 04
Mean with weights,		84 07 43	0 00

Angle from prism to brachypinacoid, B to D.

			124° 10′ 15″
No. 13, 2 f.	5	124° 13′ 30″	+ 3 15
No. 15, 2 f.	5	124 13 00	+ 2 45
No. 16, 2 p.	1	124 12 30	+ 2 15
No. 17, 2 p.	1	124 13 00	+ 2 45
No. 18, 1 g. and 1 p.	3	124 12 30	+ 2 15
No. 19, 1 v. g. and 1 f.	7	124 05 00	— 5 15
No. 20, 1 v. g. and 1 f.	7	124 09 00	— 1 15
Mean,		124 11 13	+ 0 58
Mean with weights,		124 10 07	— 0 08

Angle from prism to macrodome, B to A.

			127° 53′ 46″
No. 15, 1 g. and 1 f.	6	127° 55′ 30″	+ 1 44
No. 16, 2 f.	5	127 55 30	+ 1 44
No. 17, 1 f. and 1 p.	2	127 55 00	+ 1 14
No. 19, 1 f. and 1 p.	2	127 57 00	+ 3 14
No. 20, 2 v. g.	10	127 52 00	— 1 46
Mean,		127 55 00	+ 1 14
Mean with weights,		127 54 11	+ 0 25

The axes may be calculated from the angles 68° 20′ 30″ and 84° 07′ 43″.

The axial ratio is: a : b : c as 0.678855 : 1 : 0.752244.

Measurements of Di-ammonium Bromo-stannite, $(NH_4)_2SnBr_4.2H_2O$.

Obtuse prism angle, B to B over C.

			111° 43′ 14″
No. 23, 2 f.	5	111° 43′ 00″	— 0 14
No. 24, 2 f.	5	111 41 00	— 2 14
No. 25, 2 f.	5	111 46 00	+ 2 46
No. 26, 2 f.	5	111 41 00	— 2 14
No. 27, 2 f.	5	111 40 00	— 3 14
No. 28, 1 g. and 1 f.	6	111 45 00	+ 1 46
Mean,		111 42 40	— 0 34
Mean with weights,		111 42 44	— 0 30

Acute prism angle, B to B over D.

			68° 16′ 46″
No. 23, 2 f.	5	68° 15′ 00″	— 1 46
No. 24, 2 p.	1	68 18 00	+ 1 14
No. 25, 2 f.	5	68 17 30	+ 0 44
No. 26, 1 f. and 1 p.	2	68 13 30	— 3 16
No. 27, 2 f.	5	68 19 30	+ 2 44
No. 28, 2 f.	5	68 15 00	— 1 46
Mean,		68 16 00	— 0 36
Mean with weights,		68 16 16	— 0 30

Angle of macrodome, A to A over top.

			84° 17′ 42″
No. 23, 1 v. g. and 1 p.	4	84 30″	+ 2 48
No. 25, 2 g.	8	84 21 00	+ 3 18
No. 26, 2 g.	8	84 20 00	+ 2 18
No. 28, 2 f.	5	84 18 00	+ 0 18
No. 29, 2 v. g.	10	84 21 00	+ 3 18
No. 30, 2 g.	8	84 15 30	— 2 12
No. 31, 1 v. g. and 1 g.	9	84 14 00	— 3 42
No. 32, 2 g.	8	84 16 30	— 1 12
No. 33, 2 g.	8	84 14 00	— 3 42
Mean,		84 17 50	+ 0 08
Mean with weights,		84 17 42	0 00

Angle from the prism to the macrodome, B to A.

			127° 51′ 15″
No. 23, 1 v. g. and 1 p.	4	127° 54′ 00″	+ 2 45
No. 26, 1 g. and 1 p.	3	127 51 30	+ 0 15
No. 27, 2 f.	5	127 53 00	+ 1 45
No. 28, 2 f.	5	127 51 00	— 0 15
No. 29, 1 v. g. and 1 f.	7	127 51 00	— 0 15
No. 30, 2 g.	8	127 51 00	— 0 15
Mean,		127 51 55	+ 0 40
Mean with weights,		127 51 47	+ 0 32

Calculating the axial ratios from the angles 68° 16′ 46″ and 84° 17′ 42″, we have a : b : c as 0.678063 : 1 : 0.749178.

Measurements of Di-potassium Bromo-stannite, $K_2SnBr_4.2H_2O$.

Obtuse prism angle, B to B over C.

			111° 20′ 52″
No. 34, 2 f.	5	111° 21′ 00″	+ 0 08
No. 35, 2 p.	1	111 20 00	— 0 52
No. 36, 1 f. and 1 p.	2	111 16 00	— 4 52
No. 37, 1 f. and 1 g.	6	111 18 30	— 2 22
No. 38, 2 f.	5	111 24 00	+ 3 08
No. 39, 2 f.	5	111 20 00	— 0 52
No. 40, 1 f. and 1 p.	2	111 20 00	— 0 52
Mean,		111 19 59	— 0 53
Mean with weights,		111 20 12	— 0 40

Acute prism angle, B to B over D.

			68° 39′ 08″
No. 34, 1 f. and 1 p.	2	68° 35′ 00″	— 4 08
No. 36, 1 f. and 1 g.	6	68 45 30	+ 6 22
No. 37, 1 f. and 1 p.	2	68 40 30	+ 1 22
No. 38, 2 f.	5	68 36 00	— 3 08
No. 39, 1 v. g. and 1 g.	9	68 36 00	— 3 08
No. 41, 2 f.	5	68 38 30	— 0 38
No. 42, 2 p.	1	68 40 00	+ 0 52
Mean,		68 38 34	— 0 34
Mean with weights,		68 38 28	— 0 40

Angle of macrodome, A to A over top.

			84° 52′ 46″
No. 37, 2 p.	1	84° 48′ 00″	— 4 46
No. 39, 1 f. and 1 g.	6	84 54 00	+ 1 14
No. 42, 2 f.	5	84 53 00	+ 0 14
Mean,		84 51 40	— 1 06
Mean with weights,		84 53 05	+ 0 19

Angle from prism to pyramid, B to E.

			142° 56′ 48″
No. 37, 2 p.	1	142° 55′ 30″	— 1 18
No. 38, 2 p.	1	143 01 00	+ 4 12
No. 39, 1 f. and 1 g.	6	142 52 30	— 3 18
No. 40, 2 f.	5	143 01 00	+ 4 12
No. 42, 2 p.	1	142 54 00	— 2 18
No. 43, 2 p.	1	142 55 00	— 1 18
Mean,		142 56 45	— 0 03
Mean with weights,		142 56 48	0 00

Calculating the value of the axes from the angles 68° 39′ 08″ and 142° 56′ 48″ we get:

a : b : c as 0.682822 : 1 : 0.746746.

Collecting these results we have the following tabular statement:

	A.	C.	$\infty P \wedge \infty P$.	$P\bar{\infty} \wedge P\bar{\infty}$.
$K_2SnCl_4.2H_2O$	0.685231	0.758634	68° 50′ 25″	84° 10′ 46″
$(NH_4)_2SnCl_4.2H_2O$	0.678855	0.752244	68 20 30	84 07 43
$(NH_4)_2SnBr_4.2H_2O$	0.678063	0.749178	68 16 46	84 17 42
$K_2SnBr_4.2H_2O$	0.682822	0.746746	68 39 08	84 52 46

The changes in the value of the axes may be farther tabulated as follows:

In passing	The change in A is	The change in C is
From $K_2SnCl_4.2H_2O$ to $K_2SnBr_4.2H_2O$	— 0.002409	— 0.011888
From $(NH_4)_2SnCl_4.2H_2O$ to $(NH_4)_2SnBr_4.2H_2O$	— 0.000792	— 0.003066
From $K_2SnCl_4.2H_2O$ to $(NH_4)_2SnCl_4.2H_2O$	— 0.006376	— 0.006390
From $K_2SnBr_4.2H_2O$ to $(NH_4)_2SnBr_4.2H_2O$	— 0.004759	+ 0.002432

From this table we see that the change in the halogen or acid element appears to affect the vertical axis much more than it does the lateral axis, and that the change is much less marked with the ammonium salt than with the potassium salt.

While the change in the alkali or basic element affects both axes to nearly the same extent in the case of the chlorides, and the lateral axis more in the case of the bromides, we find that the vertical axis is *increased* instead of diminished in passing from

$K_2SnBr_6.2H_2O$ to $(NH_4)_2SnBr_6.2H_2O$. The A and C axes are both nearer unity in the chlorides than in the bromides, and in general the potassium salts approach the regular form more closely than the ammonium salts.

It is hoped to increase the number of salts in this series by preparing the rubidium and cæsium salts if possible; with the additional data thus obtained, perhaps the law governing the change in the axes will be more apparent.

II.—On the Double Halides of Lead.[1]

By Charles H. Herty.

Several double iodides of lead are described in chemical literature. Boullay[2] describes two. One of these has the composition $KPbI_3$ ($PbI_2.KI$), and the other K_4PbI_6 ($PbI_2.4KI$). In Graham-Otto's Lehrbuch der anorganischen Chemie (Bd. II, 3, p. 1189), a salt of the composition K_3PbI_7 ($PbI_2.5KI$) is mentioned. This seems, however, to be an error of the compiler of the book, as a careful search through the literature has failed to bring to light a salt of this composition. Ditte[3] describes a salt of the composition $K_2PbI_4.4H_2O$; and later Berthelot[4] gives an account of two salts of the composition $K_2PbI_4.2H_2O$ and $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$). Berthelot ascribes the latter salt to Boullay, but no account of this salt could be found in the articles of Boullay. Very little work has been done on other double halides of lead. Reference will be made below to a few articles bearing on this subject.

One of the chief difficulties encountered in this investigation was the analysis of the compounds. It was found at the outset that the methods hitherto used, and those that first suggest themselves, are not capable of yielding satisfactory results. Previous investigators mention no difficulties, and give no directions for analysis. This makes it appear probable that they used methods that cannot give good results. In spite of long continued efforts it must be confessed that as yet no absolutely trustworthy method for complete analysis has been found. The

[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1890.

[2] Ann. chim. phys. [2] **34**, 366. [3] Ibid. [5] **24**, 226. [4] Ibid. [5] **29**, 289.

composition of most of the salts prepared in this investigation was deduced from the determinations of water of crystallisation and lead. The water was determined by heating to 110° for three hours a portion of the salt thoroughly dried by pressing between drying paper. In another portion the lead was determined thus: A weighed portion of the salt (about 1 gram) was introduced into an Erlenmeyer flask of 125 cc. capacity. Sulphuric acid sufficient to decompose the salt was introduced into the flask, which was then inclined in order to prevent loss, and gentle heat applied until all the iodine was driven off. The lead and potassium were then in the form of sulphates. A close examination of the flask showed that small yellow particles of lead iodide remained undecomposed on the sides of the flask. These were washed down with concentrated sulphuric acid, and the mass thoroughly boiled for about an hour longer in order to insure the conversion of all the lead into sulphate. After cooling, the mass was diluted with water to about 100 cc. and a small quantity of alcohol added. The whole was then allowed to stand until the supernatant liquid became perfectly clear, when it was filtered through a Gooch crucible. The lead sulphate was then washed thoroughly, first with water to which a little sulphuric acid and alcohol had been added, in order to remove all traces of potassium sulphate, then with water containing a little alcohol in order to remove all sulphuric acid. The crucible was then dried thoroughly at 110° and finally heated to a low red heat, allowed to cool in a desiccator for twenty minutes and weighed. To determine the potassium by simple evaporation of the filtrate containing potassium sulphate and sulphuric acid is not practicable on account of the large excess of sulphuric acid necessarily present. Experiments were made on the separation of lead as sulphide by hydrogen sulphide, but it was found that in every case some of the lead sulphide remained in solution, in consequence of the presence of the alkali halide. Various other methods were tried, all of which proved of no value.

The method finally adopted for complete analysis is as follows:

1. In one portion of the salt, water of crystallisation was determined by heating in an air-bath for three hours at 110°.

2. In a second portion, lead was determined by conversion into the sulphate, as described above.

3. In a third portion, iodine and potassium were determined

thus: about 1 gram of the salt was treated with 100 cc. water in a small beaker. This was stirred thoroughly in order to insure complete decomposition of the salt, and filtered through a Gooch crucible *without washing*, for if water be added to the filtrate lead iodide separates. The iodine in the filtrate was then precipitated as silver iodide. The residue on the Gooch crucible was then washed with cold water, and the washings again passed through the crucible in order to retain any lead iodide which may have separated, and to insure all potassium iodide being removed from the crucible. This second filtrate was then added to the first, in which silver nitrate was present in excess. The silver iodide was then washed, dried and weighed. The lead iodide on the crucible was then dried and weighed. From the combined results of lead iodide and silver iodide the total amount of iodine was calculated.

4. The filtrate from the silver iodide was then treated with hydrogen sulphide in order to remove all lead and silver, filtered and evaporated to dryness with a little sulphuric acid. The residue of potassium sulphate was then heated to redness, allowed to cool, and weighed. From this the weight of potassium was calculated.

An analysis of one of the specimens obtained gave the following results:

I. 1.2486 grams salt lost 0.0683 gram H_2O.

II. 0.8166 gram salt gave 0.3687 gram $PbSO_4$ = 0.2518 gram Pb.

III. 1.4549 grams salt gave 0.9057 gram PbI_2 = 0.4989 gram I, and 0.622 gram AgI = 0.3361 gram I. (Total I = 0.8350 gram.)

IV. 1.4549 grams salt gave 0.2018 gram K_2SO_4 = 0.0906 gram K.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.84
I	57.43	57.39
K	5.91	6.23
H_2O	5.43	5.47

This salt was evidently the salt $KPbI_3.2H_2O$. As this analysis showed that the methods for determining water of crystallisation and lead were reliable, all the salts were identified by the determinations of these constituents. In all the calculations the atomic weights given by Meyer and Seubert were used.

Potassium Iodoplumbite.

I. *Salt of the composition* $KPbI_3.2H_2O$ ($PbI_2.KI.2H_2O$). The first work on the subject of the combinations of lead iodide with potassium iodide was done by Boullay,[1] who in 1827 announced, as the result of his work, the existence of the two salts $PbI_2.KI$ ($KPbI_3$) and $PbI_2.4KI$ (K_4PbI_6). The latter forms a very marked exception to the law of combination of the alkali halides with other halides. As the work of Boullay had been carried out quite a long time ago it was deemed advisable to repeat it, for at that time quantitative determinations were not so accurate as at present, and, furthermore, the filter-pump had not then been invented, so that the method of preparation of the salts must have been rather crude. The first efforts were therefore directed to the preparation of the salt $PbI_2.KI$ ($KPbI_3$) described by Boullay. The potassium iodide used in these experiments was purified by decomposing any iodate present by zinc amalgam.[2] The lead iodide first used was prepared by precipitating a solution of pure lead nitrate with pure potassium iodide solution. Towards the latter part of the investigation commercial lead iodide was used. This gave results agreeing very closely with those obtained by using the lead iodide prepared for the purpose.

According to Boullay, when a solution of lead nitrate is added to a slightly concentrated solution of potassium iodide there is formed at first a red precipitate of lead iodide which soon turns white, owing to the conversion of the lead iodide into the double salt $PbI_2.KI(KPbI_3)$. Great trouble was experienced at first in preparing this salt. Boullay directed to use a solution of potassium iodide only slightly concentrated. In each of the preliminary experiments lead iodide was precipitated when a solution of lead nitrate was added to a solution of potassium iodide only slightly concentrated; but, on standing, whether cold or hot, there was no change to a white color as described by Boullay. But when a solution of potassium iodide slightly more concentrated was used and heat applied, it was noticed that yellow needles formed along the upper portion of the beaker in which the experiment was being conducted, where drops of the solution had spattered, these drops becoming more concentrated by evaporation. This observation suggested that if a more concentrated solution of potassium iodide were used the salt might be obtained. Experiments were

[1] Ann. chim. phys. [2] **34**, 366. [2] This Journal **10**, 321.

then made to determine the exact conditions under which the salt is formed. Solutions of lead nitrate and of potassium iodide were prepared, each containing .25 gram of salt in 1 cc. Five portions of the lead nitrate solution of 5 cc. each were then measured out. To these were added quantities of potassium iodide solution (warm) varying from 5 cc. to 25 cc. Lead iodide was precipitated in each case, but on cooling the mass did not in any case turn white, as described by Boullay. So to five portions more (5 cc. each) of the potassium iodide solution were added successively quantities of solid potassium iodide varying from 0.25 gram to 1.25 grams. These portions were heated and added to 5 cc. portions of the lead nitrate solution. Lead iodide was precipitated in each case, but still there was no double salt formed; so, again to five portions (5 cc. each) of the potassium iodide solution were added quantities of solid potassium iodide varying from 3 grams to 5 grams. The solutions were then heated and added to five portions (5 cc. each) of the lead nitrate solution. Lead iodide was precipitated in each case, but gradually the red precipitate became white, the most concentrated solution becoming white first. On heating, the white salt was decomposed and insoluble lead iodide remained, having the form of the original crystals; but, on cooling, the crystals again became white, owing to the formation of the double salt, as described by Boullay. This slightly yellowish salt was freed from the mother-liquor as much as possible by means of a filter-pump, then pressed between drying paper and placed in a desiccator for twelve hours. The analysis gave the following results:

I. 0.9779 gram salt lost 0.0111 gram H_2O.

II. 1.6154 grams salt gave 0.7023 gram $PbSO_4$ = 0.4797 gram Pb.

III. 1.0204 grams salt, after standing over sulphuric acid one week, lost 0.0028 gram.

	Calculated for $KPbI_3$ (PbI_2.KI).	Found. I.	II.	III.
Pb	33.02	...	29.70	...
H_2O	...	1.14	...	0.273

Plainly this salt lost its water of crystallisation by standing over sulphuric acid. From the mother-liquor of this salt there crystallised after twelve hours long needles of slightly yellowish tint. By a slight elevation of temperature these needles are redissolved in the mother-liquor, but by rapidly heating the beaker containing

the mass the needles are decomposed, lead iodide remaining, which retains the form of the original crystals. On cooling these needles again became white. The explanation of the formation of these long needles in the mother-liquor will be given under the head of the salt $K_4Pb_2I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$).

The salt $KPbI_3$ ($PbI_2.KI$) was then prepared in larger quantities by using the following proportions: 4 grams of lead nitrate were dissolved in 15 cc. of water, and 15 grams potassium iodide in 15 cc. of water. The latter solution was then heated and added to the nitrate solution, which was stirred and kept cold. The double salt thus formed was pumped dry and thoroughly pressed between drying paper. The analysis of this salt gave the following results:

I. 1.3640 grams salt lost 0.0712 gram H_2O.

II. 1.1614 grams salt lost 0.0610 gram H_2O.

III. 1.0744 grams salt gave 0.4842 gram $PbSO_4$ = 0.3307 gram Pb.

IV. 1.3640 grams salt gave 0.6162 gram $PbSO_4$ = 0.4209 gram Pb.

V. 0.8867 gram salt gave 0.4002 gram $PbSO_4$ = 0.2733 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found. I.	II.	III.	IV.	V.
Pb	31.23	...	...	30.78	30.86	30.82
H_2O	5.43	5.22	5.25	...	...	...

This was evidently the salt $KPbI_3.2H_2O$. Boullay prepared this salt, but dried it over lime; accordingly he found only 3 per cent. H_2O, and says:[1] "Si l'on suppose que, dans ce sel, les deux iodures soient à l'état d'hydriodates, il foudrait 4.16 l'eau pour 100 parties du sel humide; je n'en ai trouvé que 3.00."

In speaking of the formation of this salt, Boullay states that it is always formed when a slightly concentrated solution of potassium iodide is brought together, hot or cold, with an *excess of lead iodide.* It is difficult to understand why he should have made this statement, as it is evident from his work on the subject that he never worked with an excess of lead iodide, but that in each case lead iodide was first precipitated, and this was then converted into the double salt, or rather iodoplumbite, by the excess of potassium iodide in the solution. However, in order to test his statement strictly, a solution of potassium iodide not quite saturated at 20° was added to a large excess of lead iodide in a beaker,

[1] Ann. chim. phys. [2], **34**, 367.

and stirred thoroughly. On first cooling, the excess of lead iodide collected at the bottom of the vessel, while the supernatant liquid remained clear; but on the following day silky, needle-shaped crystals were found in the solution and also mixed with unchanged lead iodide in the bottom of the vessel. The best crystals were removed from the solution, dried and analysed, giving the following results:

0.2150 gram salt gave 0.0957 gram $PbSO_4$ = 0.0654 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.42

This was therefore the same salt as has been previously prepared.

Some of the needle-shaped crystals of the salt $KPbI_3.2H_2O$ were then heated to 140° to test whether any more water could be driven off than at 110°, but no further loss of weight was found. The further effect of heat upon this salt was tried in this way. Some of the needle-shaped crystals were placed in an ignition tube; this in turn was placed in a sulphuric acid bath and the temperature raised gradually. At 70° water began to be given off, the salt becoming a brighter yellow and decreasing considerably in bulk. As the temperature was raised the amount of water given off increased to such an extent that it collected in large drops on the side of the tube. These drops falling on the salt below decomposed it instantly, as was shown by the color of the lead iodide which appeared. Thus the same water which had been present in the compound as water of crystallisation, after having been once driven out by heat, served to decompose the anhydrous salt when brought in contact with it. By using an ignition tube, bent at an angle in order to prevent the water falling back upon the salt, it was found that at about 310° the salt decomposed, iodine being given off. Treated with absolute alcohol, this salt is decomposed just as when treated with water.

II. *Salt of the composition* K_4PbI_6 ($PbI_2.4KI$). — While attempting to determine the concentration at which the salt $KPbI_3.2H_2O$ was formed, as mentioned above, efforts were made to prepare the salt K_4PbI_6 ($PbI_2.4KI$) described by Boullay[1] under the head of "Bibasic iodoplumbate of iodide of potassium." He obtained it by adding lead iodide to a concentrated solution of potassium iodide, this last being in excess. He represented

[1] Ann. chim. phys. [2] **34**, 370.

the composition of the salt by the formula "$2KaI_4 + PbI_4$," or, according to the present atomic weights, $PbI_2 + 4KI$. This formula was based upon the following analyses:

	Found. I.	Found. II.	Calculated for $PbI_2 + 4KI$.
PbI_2	34.0	36.0	41.0
KI	66.0	64.0	59.0

To a cold saturated solution of potassium iodide lead nitrate was added, and a yellowish white salt was obtained. This was the first compound of lead and potassium iodides obtained during the course of the investigation, and was dried not by pumping off the mother-liquor, but by simple filtration, then pressing between drying paper for a short time, and finally completely dried by standing over lime, the method adopted by Boullay.

On analysis this salt showed:

I. 1.2961 grams salt lost 0.0388 gram H_2O.

II. 1.2734 grams salt lost 0.0191 gram H_2O.

III. 0.3880 gram salt gave 0.1435 gram $PbSO_4 = 0.0980$ gram Pb.

IV. 2.3640 grams salt gave 0.9015 gram $PbSO_4 = 0.6157$ gram Pb.

	Calculated for $PbI_2.4KI$.	Found. I.	Found. II.	Found. III.	Found. IV.
Pb	18.40	...	...	25.26	26.04
H_2O	...	2.99	1.50	...	...

These results plainly show that the salt K_4PbI_6 ($PbI_2.4KI$) had not been obtained, but rather a salt approaching in composition the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) described by Ditte,[1] with the exception of the water, which showed by the difference in the two analyses, the second having been made several days after the first, that water was abstracted by the lime over which the salt stood. The preparation of this salt and its analyses were rather crude, as they were the first attempts; however, the results were sufficient to show that the salt K_4PbI_6 ($PbI_2.4KI$) had not been obtained under the conditions described by Boullay. Later in the investigation, after skill in dealing with these compounds had been acquired, another attempt was made to prepare the salt, following the directions of Boullay, with the exception that the salt, instead of being dried over lime, was pressed for several days between drying paper. On analysis this salt showed:

[1] Ann. chim. phys. [5] 24, 226.

I. 1.2106 grams salt lost 0.0634 gram H_2O.

II. 0.9371 gram salt lost 0.0490 gram H_2O.

III. 1.0085 grams salt gave 0.4569 gram $PbSO_4$ = 0.3121 gram Pb.

IV. 0.8693 gram salt gave 0.3914 gram $PbSO_4$ = 0.2673 gram Pb.

	Calculated for		Found.			
	K_4PbI_6.	$KPbI_3.2H_2O$.	I.	II.	III.	IV.
Pb	18.40	31.23	...	...	30.95	30.75
H_2O	...	5.43	5.24	5.23	...	...

The salt was evidently the salt $KPbI_3.2H_2O$. These last results differ very widely from those first obtained in trying to prepare the salt K_4PbI_6; in the first case the percentage of lead is 25.26, in the second case 30.95. Many efforts were then made to obtain the salt which showed 25.26 per cent. of lead, varying the conditions in all possible ways, but in no case was a salt obtained even approaching this composition. Therefore it seems justifiable to conclude that the salt yielding 25.26 per cent. of lead which was prepared and analysed in a rather rough way, must have been very impure, owing to excess of potassium iodide present. From the above facts it appears to follow that the salt K_4PbI_6 ($PbI_2.4KI$) does not exist, and that the mass which Boullay considered to have this composition was a mixture of the salt $KPbI_3.2H_2O$ with a large excess of potassium iodide.

III. *Salts of the composition* $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) and $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$).—Since the paper published by Boullay in 1827, the principal work on the double iodides of lead and potassium has been done by Ditte, and also by Berthelot. Ditte[1] described the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$), giving an account of its method of formation, appearance and general behavior, and studied its decomposition by water.

Berthelot[2] then took up the subject and described the two salts, $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$) and $K_4Pb_2I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$). This investigation was now directed to the repetition of the work of these chemists. Both agree that the salt containing lead and potassium iodides, in the proportion of one part of lead iodide to two parts of potassium iodide, is formed whenever lead iodide is added to a warm solution of potassium iodide and the solution allowed to cool. Ditte states that the salt is formed also in the cold.

[1] Ann. chim. phys. [5] **24**, 226.

[2] Ann. chim. phys. [5], **29**, 289.

As previously stated, when this investigation was first begun a salt was obtained which seemed to have the composition $K_2PbI_4 + H_2O$ ($PbI_2.2KI + H_2O$), the water of crystallisation not being constant. But now, on the first attempt to repeat the work of Ditte, a salt was obtained resembling in appearance that described by him, but on analysis it gave the following results:

I. 1.2227 grams salt lost 0.0413 gram H_2O.

II. 2.1526 grams salt gave 0.9541 gram $PbSO_4 = 0.6517$ gram Pb.

III. 0.9733 gram salt gave 0.4296 gram $PbSO_4 = 0.2934$ gram Pb.

	Calculated for		Found.		
	$K_2PbI_4.4H_2O$.	$KPbI_3.2H_2O$.	I.	II.	III.
Pb	23.93	31.23	...	30.28	30.14
H_2O	8.33	5.43	3.38	...	...

Evidently this salt agreed more closely with the formula $KPbI_3.2H_2O$ than $K_2PbI_4.4H_2O$. The water of crystallisation varied in this salt, as it was dried over lime, as was the case with several of the preceding salts. The salt just mentioned was prepared from a hot solution. As it had been shown earlier that heat decomposed the salt $KPbI_3.2H_2O$ with separation of lead iodide, it was thought probable that the salt $K_2PbI_4.4H_2O$ might be prepared in the cold. To this end 15 cc. of a cold saturated solution of potassium iodide was added to 10 cc. of a cold saturated solution of lead nitrate. The lead iodide first precipitated soon turned white, owing to the formation of the double salt. The mass having become quite pasty, more of the potassium iodide solution was added, enough to render the mass quite mobile and to insure the conversion of all lead iodide into the double salt. The salt prepared in this way was analysed by boiling with sodium carbonate, the lead iodide being thus changed to the carbonate. This was then filtered through a Gooch crucible, washed thoroughly and ignited at a low red heat. The lead was then weighed as oxide. Analysed in this way the following results were obtained:

I. 1.7823 grams salt lost 0.0966 gram H_2O.

II. 1.6530 grams salt lost 0.0892 gram H_2O.

III. 1.7823 grams salt gave 0.5990 gram $PbO = 0.5560$ gram Pb.

	Calculated for		Found.		
	$K_2PbI_4.4H_2O$.	$KPbI_3.2H_2O$.	I.	II.	III.
Pb	23.93	31.23	...	...	31.20
H_2O	8.33	5.43	5.42	5.39	...

As the effort to prepare the salt $K_2PbI_4.4H_2O$ in the cold had failed, it was then attempted to prepare it by heating a cold saturated solution of potassium iodide almost to boiling, then adding lead iodide to saturation; but this was found impracticable, since such large quantities of lead iodide are taken up by the solution that the double salt begins to separate from the solution at the surface while lead iodide is still being dissolved. So to a hot solution of potassium iodide (cold saturated) lead iodide was added in large quantities, but not enough to cause the separation of the double salt, as mentioned above. On cooling, pale yellow needles separated. These were dried and marked No. 1. The filtrate from this salt was moderately diluted with water, and soon light-colored needle-shaped crystals were seen to appear. On standing for a short time the whole mass became almost solid, owing to the thick network of crystals formed. These were dried and marked No. 2. By continuing the dilution crystals again began to appear, but now on adding more water these crystals were decomposed into lead iodide and potassium iodide. However, on stirring the mass thoroughly the original white color was restored. These crystals were dried and marked No. 3. By further dilution of the filtrate still another crop of crystals were obtained. These were dried and marked No. 4. On adding water to a small portion of the filtrate, decomposition took place immediately, lead iodide separating in large quantities. But on treating another portion of the filtrate with alcohol a flocculent white salt separated, which on close examination seemed to be composed of little needles. These were dried and marked No. 5. It was thought that these five salts would prove to be a series of compounds showing a gradation in composition. On analysis these salts gave the following results:

I. 1.5388 grams of salt No. 1 lost 0.0813 gram H_2O, and 1.6216 grams of salt No. 1 gave 0.7300 gram $PbSO_4 = 0.4986$ gram Pb.

II. 1.2032 grams salt No. 2 lost 0.0617 gram H_2O, and 1.1969 grams salt No. 2 gave 0.5391 gram $PbSO_4 = 0.3682$ gram Pb.

III. 1.2780 grams salt No. 3 lost 0.0673 gram H_2O and gave 0.5782 gram $PbSO_4 = 0.3949$ gram Pb.

IV. 1.1226 grams salt No. 4 lost 0.0590 gram H_2O and gave 0.5096 gram $PbSO_4 = 0.3481$ gram Pb.

V. 1.2413 grams salt No. 5 lost 0.0639 gram H_2O and gave 0.5637 gram $PbSO_4 = 0.3850$ gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found. I.	II.	III.	IV.	V.
Pb	31.23	30.75	30.76	30.90	31.01	31.02
H_2O	5.43	5.28	5.13	5.27	5.26	5.15

The results here, as in almost all of the analyses, are below the theoretical. This is to be expected, as the mother-liquor, which is rich in potassium iodide, cannot be washed from the salts, but has to be removed by pressing between drying paper. This would plainly lead to low results for water and lead, and at the same time high results for iodine and potassium.

An examination of the above results shows that instead of obtaining a series of salts the same salt was obtained in every case, becoming gradually purer as the solution was diluted. Boullay observed this same phenomenon. These facts also show that the same salt, $KPbI_3.2H_2O$, is obtained, and not the salt $K_2PbI_4.4H_2O$, described by Ditte, whether a hot concentrated or a cold solution of potassium iodide be used, decreasing from considerable concentration to just above the point where separation of lead iodide takes place; and still further, alcohol separates the same salt from this last most dilute solution. This is very strong evidence against the existence of the salt $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$), described by Ditte, or $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$), described by Berthelot.

Another solution was then prepared similar to that from which the salt marked No. 1 had been obtained, but instead of filtering from the crystals formed, water was added. Lead iodide at first separated, but by stirring the mass thoroughly the original color was restored. In this way a large quantity of water was added, until finally, by further addition of water to a small portion of the mass, lead iodide was seen to separate, and remained undissolved even after thorough stirring. The analysis of the salt thus formed proved it to be the salt $KPbI_3.2H_2O$.

Efforts were then made to prepare the salt $K_2PbI_4.4H_2O$ by dissolving the salt $KPbI_3.2H_2O$ in a large excess of a cold saturated solution of potassium iodide. On heating, the salt dissolved, and on cooling, long needle-shaped crystals separated, similar in appearance to the salt which had been dissolved. On analysis this salt gave the following results:

I. 1.0974 grams salt gave 0.4942 gram $PbSO_4$ = 0.3375 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found.
Pb	31.23	30.75

On following the directions of Ditte[1] in every detail a salt was prepared which, when heated before being separated from its mother-liquor, decomposed. The lead iodide so formed retained the form of the original crystals. On filtering now and allowing to cool, a network of needle-shaped crystals was obtained which almost completely filled the solution. On analysis this salt gave the following results:

I. 1.2172 grams salt lost 0.0650 gram H_2O.

II. 0.8487 gram salt gave 0.3836 gram $PbSO_4$ = 0.2620 gram Pb.

	Calculated for		Found.	
	$KPbI_3.2H_2O$.	$K_2PbI_4.4H_2O$.	I.	II.
Pb	31.23	23.93	...	30.87
H_2O	5.43	8.33	5.34	...

This was evidently the same salt which had been obtained in all the previous experiments.

Ditte[2] describes another method for the preparation of the salt $K_2PbI_4.4H_2O$. As all previous efforts to prepare the salt had failed, it was thought that possibly by this means the salt might be obtained, or, on the other hand, conclusive evidence obtained that the salt does not exist.

This method of preparation consists in mixing freshly precipitated lead carbonate with an excess of a cold saturated solution of potassium iodide. No action takes place at ordinary temperatures, but on passing a current of carbon dioxide through the mixture for about twenty minutes the white lead carbonate is replaced by the yellowish crystals of the double salt. A salt prepared in this way gave on analysis the following results:

I. 0.9316 gram salt lost 0.0492 gram H_2O.

II. 1.0653 grams salt gave 0.4908 gram $PbSO_4$ = 0.3352 gram Pb.

III. 0.8595 gram salt gave 0.3958 gram $PbSO_4$ = 0.2703 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	I.	Found. II.	III.
Pb	31.23	...	31.47	31.45
H_2O	5.43	5.28	...	...

It is clear that this method for the preparation of the salt $K_2PbI_4.4H_2O$ also failed.

The salt $K_2PbI_4.2H_2O$ described by Berthelot[3] was obtained,

[1] Ann. chim. phys. [5] **24**, 226. [2] Ibid. [5] **24**, 235. [3] Ibid. [5] **29**, 289.

to use his own words, "par le froidissement de la solution de l'iodure de plomb dans une solution concentrée d'iodure de potassium." Plainly this condition has been tried repeatedly in the effort to prepare the salt $K_2PbI_4.4H_2O$ (Ditte), but in order to be absolutely certain that this salt of Berthelot could not be prepared, three successive attempts were made, varying the conditions slightly in each case. The salts obtained in this way gave on analysis the following results:

I. 1.0975 grams salt No. 1 lost 0.0565 gram H_2O, and 1.3778 grams salt No. 1 gave 0.6141 gram $PbSO_4$ = 0.4194 gram Pb.

II. 1.3876 grams salt No. 2 lost 0.0724 gram H_2O, and 0.6197 gram salt No. 2 gave 0.2738 gram $PbSO_4$ = 0.1870 gram Pb.

III. 0.9158 gram salt No. 3 lost 0.0477 gram H_2O, and 0.8046 gram salt No. 3 gave 0.3569 gram $PbSO_4$ = 0.2438 gram Pb.

	Calculated for		Found.		
	$K_2PbI_4.2H_2O$.	$KPbI_3.2H_2O$.	I.	II.	III.
Pb	24.97	31.23	30.44	30.18	30.30
H_2O	4.35	5.43	5.15	5.22	5.21

The results show that all three salts have the composition $KPbI_3.2H_2O$. Solutions of potassium iodide saturated at 100° were then used, but were soon found to be of no value, as, when a rather small quantity of lead iodide was added, on cooling, a large mass of potassium iodide crystallised out along with the double salt; and when a large quantity of lead iodide was added the mass soon became unmanageable, on account of the large amount of double salt present in the solution, so that it could not be filtered or purified in any way.

From all of the above facts it is to be concluded that the salts $K_2PbI_4.4H_2O$ ($PbI_2.2KI.4H_2O$) and $K_2PbI_4.2H_2O$ ($PbI_2.2KI.2H_2O$) cannot be made; for not only have the directions of both Ditte and Berthelot been closely followed, but, furthermore, the conditions have been changed, using at one time hot solutions, at another cold, at one time cold saturated, at another dilute; again a solution of potassium iodide saturated at 100° was employed, and in every case the salt $KPbI_3.2H_2O$ was obtained. Further, the attempt was made to obtain the salt by dissolving the salt $KPbI_3.2H_2O$ in a cold saturated solution of potassium iodide, and finally by passing carbon dioxide through a mixture of lead carbonate and potassium iodide solution, and here likewise was obtained the salt $KPbI_3.2H_2O$.

IV. *Salt of the composition* $K_4Pb_3I_{10}.6H_2O$ ($3PbI_2.4KI.6H_2O$).—This salt was described by Berthelot.[1] He in turn ascribes it to Boullay, but gives no reference to any article by Boullay. Accordingly, careful search was made for Boullay's description of this salt while looking for his account of the salt K_5PbI_7 ($PbI_2.5KI$), mentioned above, but this search was unsuccessful.

Berthelot states that it is formed by slow cooling of the mother-liquor from the salt $K_2PbI_4.2H_2O$, which, in turn, is prepared by adding lead iodide to a concentrated solution of potassium iodide. These directions were closely followed. The mother-liquor from the salt which first separated on cooling was surrounded by water in order to lower the temperature, and was then allowed to stand four days. Long, yellow needles separated which on analysis gave the following results:

I. 0.7839 gram salt lost 0.0382 gram H_2O.

II. 0.9913 gram salt gave 0.4012 gram $PbSO_4$ = 0.2740 gram Pb.

	Calculated for $K_4Pb_3I_{10}.6H_2O$.	Calculated for $K_2Pb_2I_9.4H_2O$.	Found. I.	Found. II.
Pb	28.82	27.75	...	27.64
H_2O	5.02	4.83	4.87	...

This analysis seemed to show that the salt had the composition $K_5Pb_2I_9.4H_2O$ ($2PbI_2.3KI.4H_2O$). In order to confirm this the experiment was repeated. The mother-liquor in this case was surrounded by ice. Long needles crystallised from the solution, but in addition, considerable quantities of potassium iodide also separated. So the whole was heated gently until all had passed into solution, and then allowed to cool. The following night was very cold, and on examining the beaker the next morning there could be seen both the double salt and potassium iodide. This was heated again until all dissolved, and after several trials at different temperatures, finally a good crop of long needle-shaped crystals was obtained which were apparently free from potassium iodide. This salt on analysis showed:

I. 1.2129 grams lost 0.0647 gram H_2O.

II. 0.6945 gram salt gave 0.3140 gram $PbSO_4$ = 0.2145 gram Pb.

	Calculated for $KPbI_3.2H_2O$.	Found. I.	Found. II.
Pb	31.23	...	30.88
H_2O	5.43	5.33	...

[1] Ann. chim. phys. [5] **29**, 289.

These results showed that most probably in the first preparation of the salt the temperature was reduced too low, so that the salt was mixed with potassium iodide. In order to test this view and confirm the last experiment the work was very carefully repeated, accurate measurements being made at each stage, as follows: 100 cc. of a solution (saturated at 22°) was heated. When the temperature reached 75° lead iodide was added gradually while the temperature was being raised to 100°. In this way 17.5084 grams were added. The solution was then allowed to cool. At 34° needle-shaped crystals began to separate. The cooling was continued until the temperature reached 22°. The mother-liquor was then pumped off and placed under a bell-jar, where it was allowed to stand three days, the temperature varying only slightly above or below 18°. Long, needle-shaped crystals separated as before, and apparently free from potassium iodide. On analysis this salt showed:

I. 0.9263 gram salt lost 0.0474 gram H_2O.

II. 1.2400 grams salt gave 0.5548 gram $PbSO_4$ = 0.3789 gram Pb.

	Calculated for $K_4Pb_3I_{10}.6H_2O$.	Calculated for $KPbI_3.2H_2O$.	Found. I.	Found. II.
Pb	28.82	31.23	...	30.56
H_2O	5.02	5.43	5.12	...

From these facts it seems probable that the salt described by Berthelot as $3PbI_2.4KI.6H_2O$ ($K_4Pb_3I_{10}.6H_2O$) was really a mixture of the salts $KPbI_3.2H_2O$ and potassium iodide. Indeed this is rendered almost certain when it is remembered that at the temperature and concentration used the potassium iodide, which is present in the solution in large excess, separates very easily, as has already been shown.

Sodium Iodoplumbite, $NaPbI_3$.

The literature on this subject is very limited. Boullay[1] states that it is probable that the other alkali iodides would act like potassium iodide in regard to the formation of the double halide, but makes no experiments on the subject. Ditte[2] dismisses the subject by stating that sodium iodide behaves like potassium iodide, but gives no experimental data. Poggiale[3] mentions a double iodide of lead and sodium, to which he ascribes the

[1] Ann. chim. phys. [2] **34**, 372. [2] Compt. rend. **92**, 1343.
[3] J. prakt. Chem. **35**, 329.

formula $PbI_2.NaI$ ($NaPbI_3$). Efforts were first made to obtain this salt. For this purpose 100 grams of sodium iodide were dissolved in 75 cc. water at 20°. Lead iodide was then added until no more would dissolve, about 60 grams being thus added. This solution, on standing, deposited no crystals. The double salt is therefore much more soluble than the corresponding potassium salt. The solution was then heated and 10 grams more of lead iodide added. On cooling, nothing crystallised out, so the solution was then evaporated to about two-thirds of its former volume. On cooling, small needle-shaped crystals separated, closely resembling in appearance the potassium salt. These crystals formed in such large quantities that the mass almost completely solidified. Like the potassium salt this salt is decomposed by water and also by heat with separation of lead iodide. Great difficulty was experienced in purifying this salt, for such large quantities of sodium iodide were mixed with it. Various methods for purification were tried; for example, as sodium iodide is very deliquescent, it was hoped that by allowing the mixture to stand exposed to moist air, enough water would be taken up to dissolve the sodium iodide and leave the double salt behind, but this proved unsuccessful. The method finally adopted was as follows: The mixture was exposed to the air until a considerable quantity of water had been absorbed. The undissolved portion, on being pressed with a stirring rod, was found to contain hard granular crystals of sodium iodide. Gentle heat was then applied, and it was soon found that the granular crystals had disappeared, a bright yellow salt remaining. The heating was now discontinued and the mass filtered rapidly by means of a filter-pump (for if the heating be continued the whole passes into solution). The salt was then pressed between drying paper for several days, and at the end of that time was found still to be moist, showing that the salt itself is deliquescent. It was then dried in an air-bath at 110°. The anhydrous salt, which is reddish yellow, gave on analysis the following results:

I. 0.8511 gram salt gave 0.4326 gram $PbSO_4$ = 0.2955 gram Pb.

	Calculated for $NaPbI_3$.	Found.
Pb	33.89	34.71

The composition of the salt is therefore very probably $NaPbI_3$. Nothing definite can be said in regard to the water of crystallisation, as the salt is so deliquescent that it cannot be obtained dry at ordinary temperatures.

Potassium Bromoplumbite, $KPbBr_3.H_2O$.

The only work on this subject up to the present time is that done by Berthelot.[1] This was very unsatisfactory, however, and indeed he remarks that the substances obtained by him are not to be regarded as true chemical compounds, but as mixtures of the double salt with potassium bromide or lead bromide. He gives, however, the composition of one salt obtained as $3PbBr_2.2KBr$. Efforts were made to determine whether a definite compound of lead and potassium bromides could be obtained. It was found that if to a solution of potassium bromide (saturated at 20°) a solution of lead nitrate (saturated at 20°) be added drop by drop, the lead bromide so formed was dissolved on constant stirring until quite a large quantity had been dissolved, though not nearly so large a quantity as in the case of the iodides. When all the lead bromide possible had been dissolved the solution was allowed to stand, and in a few hours colorless crystals began to appear. After several days these tabular crystals grew to considerable size. The finely powdered salt gave on analysis the following results:

I. 0.7823 gram salt lost 0.0276 gram H_2O.

II. 1.1592 grams salt lost 0.0404 gram H_2O.

III. 1.2551 grams salt gave 0.7497 gram $PbSO_4$=0.5120 gram Pb.

IV. 0.9297 gram salt gave 0.5570 gram $PbSO_4$=0.3804 gram Pb.

	Calculated for $KPbBr_3.H_2O$.	Found. I.	II.	III.	IV.
Pb	41.06	...	...	40.80	40.92
H_2O	3.57	3.53	3.49	...	...

This salt was repeatedly prepared afterwards and the analyses leave no doubt that the composition is $KPbBr_3.H_2O$. The form of the crystals was the same in every case.

Similar efforts were made to prepare the corresponding sodium bromoplumbite, but without success. It was thought at one time that the salt had been obtained, as lath-shaped crystals separated from the solution of lead bromide in sodium bromide. This salt, however, proved on analysis to be lead bromide. Efforts were also made to prepare the salt by using a hot sodium bromide solution, but the salt which separated on cooling proved to be

[1] Ann. chim. phys. [5] **29**, 293.

lead bromide. The salt appears to be formed in solution, but as yet it has been found impossible to isolate it.

Potassium Chloroplumbite, $KPbCl_3$.

The statements made by Berthelot[1] in regard to this salt are as indefinite as those which he makes in regard to the bromoplumbite. Strohecker[2] also mentions the existence of double salts of lead and potassium chlorides, but gives no formulas.

The investigation was turned to the preparation of this salt, potassium chloroplumbite. A cold saturated solution of potassium chloride was heated to boiling and a solution of lead nitrate (cold saturated) added drop by drop, the mass being continually stirred. Lead chloride was dissolved, but not so much of the lead salt as in the case of the iodide and bromide. On cooling, a salt crystallised out in fine white needles, which on analysis gave the following results:

I. 1.2142 grams salt gave 1.0281 grams $PbSO_4$=0.7022 gram Pb.

II. 1.2039 grams salt gave 1.0176 grams $PbSO_4$=0.6950 gram Pb.

		Found.	
	Calculated for $KPbCl_3$.	I.	II.
Pb	58.71	57.81	57.73

There is no water of crystallisation in this salt. If the solution be cooled slowly and kept at about 35° the potassium chloroplumbite can be obtained in lenticular crystals, somewhat needle-shaped. These crystals have the same composition as the salt already mentioned above, but they contain some water mechanically held in the crystals, for on heating to about 200° the salt decrepitates just as potassium chloride does when heated. This salt is necessarily impure on account of the large excess of potassium chloride present in the solution.

All efforts to prepare the sodium chloroplumbite failed. A salt crystallising in radiating leaflets was obtained, but this by analysis was proved to be lead chloride.

The work on the fluorplumbites could not be carried to any extent on account of lack of time, but a few qualitative experiments showed that if a cold saturated solution of lead nitrate be added to a cold saturated solution of potassium fluoride, heated almost to boiling, a small portion of the lead fluoride so formed is

[1] Ann. chim. phys. [5] **29**, 293. [2] Jahresbericht, 1869, 282.

dissolved. Less of the lead salt is dissolved in this case, however, than in the case of either the iodide, bromide, or chloride.

It was hoped that the investigation could be extended to the mixed halides, but want of time prevented this.

Conclusion.

The principal results of this investigation may be summed up as follows:

I. Of the five iodoplumbites of potassium described by Boullay, Ditte and Berthelot, only one exists. This is the salt $KPbI_3.2H_2O$.

II. The bromoplumbite of potassium is a well crystallised compound, having the composition $KPbBr_3.H_2O$.

III. The chloroplumbite of potassium can also be prepared in well formed crystals, and has the composition $KPbCl_3$.

IV. The quantity of the lead halide dissolved in the alkaline halide increases with the atomic weight of the halogen. Only a small quantity of lead fluoride dissolves in a solution of potassium fluoride, a larger quantity of lead chloride in potassium chloride solution, a still larger quantity of lead bromide in potassium bromide solution, and greatest of all, lead iodide in potassium iodide solution.

V. The corresponding sodium salts, if formed, are separated with great difficulty, as in the case of the iodoplumbite, while no salt was isolated in the case of the sodium bromo or chloroplumbite.

VI. All these salts are decomposed by water, and in order that they may exist in solution a certain minimum amount of alkali halide must be present, this amount varying inversely as the atomic weight of the halogen atom present in the compound.

VII. The amount of the water of crystallisation decreases with the atomic weight of the halogens, thus: $KPbI_3.2H_2O$, $KPbBr_3.H_2O$, and $KPbCl_3$.

VIII. Finally, it is seen that the composition of all these salts can be expressed by formulas in which two halogen atoms play the part of the so-called linking oxygen atom, thus proving these salts to be no exception to the law of combination of alkali halides with other halides put forward by Professor Remsen.

III.—On Some Double Halides of Manganese.[1]

By Charles E. Saunders.

The following is a list of the salts hitherto described containing manganous chloride, combined with the chloride of some alkali metal (or of ammonium):

$NH_4MnCl_3.2H_2O$
$(NH_4)_2MnCl_4.H_2O$
$(NH_4)_2MnCl_4.2H_2O$
Rb_2MnCl_4
$Rb_2MnCl_4.3H_2O$
Cs_2MnCl_4
$Cs_2MnCl_4.3H_2O$
$2(Cs_2MnCl_4).5H_2O.$

Each of the salts in this very irregular series will be considered in detail in its proper connection. There is, however, a salt which should be considered before taking up the compounds in this list and those closely related to them.

Manganous Chloride, $MnCl_2.2H_2O$.

In attempting to prepare a double chloride of manganese and lithium, and also of manganese and magnesium, a substance was obtained which proved to be manganous chloride with two molecules of water of crystallisation instead of four, which is the normal number. The new form of the substance was obtained by adding a considerable quantity of ordinary manganous chloride to a concentrated solution of lithium chloride in water, then evaporating somewhat and allowing to cool. When magnesium chloride was used instead of lithium chloride, either alcohol containing water, or water alone served as the solvent, a few drops of hydrochloric acid being usually added. When magnesium chloride is present there must be added a considerable excess of manganous chloride, or a double salt will be produced instead of the simple chloride. Manganous chloride, as thus obtained, crystallised in beautiful pink crystals, usually about one centimeter in length and quite slender. The ends of the crystals were frequently hollow for some distance inward. They usually formed radiating groups,

[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1891.

but were sometimes obtained in perfectly definite crossed twins. The substance acts in general like ordinary manganous chloride, except that, as would be expected, it does not lose water of crystallisation when dried over calcium chloride, while the ordinary form loses two of its four molecules under these conditions. Analysis showed that the same salt was obtained from a solution containing lithium chloride as from one containing magnesium chloride. From the conditions of formation a pure product could not, however, be expected. The analyses here given were made first with a sample which had been dried between filtering paper, and, second, with one dried to constant weight over calcium chloride.

Analysis of salt dried between filtering paper gave the following results:

0.3924 gram salt gave 0.6753 gram AgCl (42.56 per cent. Cl), and 0.1788 gram Mn_3O_4 (32.82 per cent. Mn).

When dried over calcium chloride the salt gave the following figures on analysis:

0.3346 gram salt gave 0.5902 gram AgCl (43.62 per cent. Cl), and 0.1581 gram Mn_3O_4 (34.03 per cent. Mn).

0.2975 gram lost at 105°–110° 0.0326 gram H_2O = 10.96 per cent. H_2O.

At higher temperatures further, but slow, loss was observed, no doubt due to decomposition of the salt.

FIG. 1.

	Calculated for $MnCl_2.2H_2O$.		Found. In dried salt.	Found. In undried salt.
Mn	54.80	33.94	34.03	32.82
2Cl	70.74	43.81	43.62	42.56
H_2O	17.96	11.125	10.96	
H_2O	17.96	11.125		
	161.46	100.000		

It is evident, therefore, that the salt has the formula $MnCl_2.2H_2O$, and loses one molecule of water at 105°.

Crystallography of the salt.—It crystallises in slender prisms (Fig. 1), which were shown by their optical properties and angular measurements to be monoclinic. The crystals were usually hollow towards the end, so that the basal plane was very imperfectly developed. On this account the crystallographic angle β was found (roughly)

by measurement on a petrographical microscope, the crystal resting on one of the clinopinacoids. The other angle was measured on a Fuess goniometer. The forms observed were:

$$c = 0P, [001].$$
$$m = \infty P, [110].$$
$$b = \infty P \bar{\infty}, [010].$$

The angles measured were: $m : m = 100° 45'$, and $\angle\beta = 42°$ (nearly). From these data, taking $\bar{b}$ as unity, we have $\dot{a} = 1.238$ (nearly).

The substance sometimes forms crossed twins in which the basal plane is the twinning plane. An orthographic projection of such a twin is shown in Fig. 2.

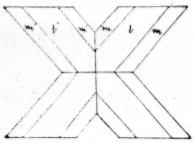


FIG. 2.

It seems probable that the magnesium chloride, or lithium chloride, present when manganous chloride crystallises out with only two molecules of water must act as a sort of dehydrating agent; and it is not unlikely that the presence of such salts as these in solutions in other cases would lead to the formation of crystals of various substances, containing less than their normal number of molecules of water.

Experiments with Potassium Chloride, etc.

On adding potassium chloride to a hot aqueous solution of manganous chloride, sufficiently concentrated to deposit crystals on cooling, a considerable amount of the alkali chloride is dissolved. When the solution cools crystals of a double chloride are deposited, which are pale pink in color, and usually form radiating groups. The individual crystals are elongated and very thin as produced in this way; but by spontaneous evaporation of the solution they can be obtained in much larger form. They are very soluble in water, but cannot be recrystallised in the ordinary sense of the term, for their solution gives a deposit of potassium chloride only, until the manganous chloride is present in large excess. This decomposition of the salt occurs in the same way in the presence of hydrochloric acid, and seems to depend merely on the different solubilities of the two constituents.

The salt is deliquescent in moist air, and was therefore dried in

a desiccator over calcium chloride before analysing. It seems to retain its water of crystallisation under these conditions, though a slow loss in weight continues, probably due to the giving up of two molecules of water of crystallisation by the manganous chloride mechanically mixed with the salt. The presence of this manganous chloride accounts for the lack of agreement between the percentage composition found and that calculated. As manganous chloride retains one molecule of water at 110°, the analysis of the salt could not be expected to give figures adding up quite to 100 per cent.

The method used for the determination of the potassium and manganese was as follows: The manganese was precipitated as carbonate by means of ammonium carbonate and then burned to mangano-manganic oxide, while the filtrate was evaporated and the potassium weighed as chloride, after subliming off the ammonium chloride. The same method was used in the case of the rubidium and cæsium salts. Here it has the great advantage of giving the alkali metal back again in the desired form. The precipitation of manganese by ammonium carbonate was found to be almost absolutely complete. Where the filtrate containing the alkali chloride was evaporated in glass vessels, a blank experiment, performed under similar conditions, gave the amount of glass dissolved, which was then deducted.

0.4562 gram salt gave 0.1479 gram Mn_3O_4 (23.35 per cent. Mn), and 0.1415 gram KCl (16.27 per cent. K).

0.2969 gram salt gave 0.5388 gram AgCl (44.88 per cent. Cl.)

0.2517 gram salt lost at 105°–110° 0.0381 gram H_2O = 15.14 per cent. H_2O.

	Calculated.		Found.
K	39.03	16.55	16.27
3Cl	106.11	44.99	44.88
Mn	54.8	23.23	23.35
$2H_2O$	35.92	15.23	15.14
	235.86	100.00	99.64

The salt has therefore the formula $KMnCl_3.2H_2O$. It has not been previously described. All efforts to obtain a salt containing a larger proportion of potassium chloride failed. No iodide or fluoride of manganese and potassium was obtained, nor was a bromide obtained by itself, though the substance described below may be regarded as containing a simple double bromide.

Efforts were made to produce, if possible, mixed salts (a chlor-bromide and a chlor-iodide) of definite composition. These experiments will now be described.

If a hot, saturated solution of manganous chloride be saturated with potassium bromide and then allowed to cool, crystals are deposited exactly similar in appearance to those of the salt $KMnCl_3.2H_2O$, but containing a considerable amount of bromine. On evaporation of the solution further deposits of crystals can be obtained. The percentage of bromine was found to vary in different crystallisations, as shown by the following analyses, the first being of a very early deposit and the second of a much later one:

I. 0.7380 gram of the salt was dissolved in 500 cc. of water and divided into two equal parts. In each portion the chlorine was precipitated as silver chloride, one of the precipitates being collected and weighed in a Gooch crucible, while the other was reduced to metallic silver in a current of hydrogen.

0.3690 gram gave 0.6621 gram $AgCl + AgBr$, and 0.4823 gram Ag. Hence $Br = 0.03836$ gram $= 10.40$ per cent., and $Cl = 0.14144$ gram $= 38.33$ per cent.

II. The amount of silver which a given weight of the salt would precipitate was determined volumetrically (by Mohr's method), and, in a separate portion, the weight of the mixed precipitates formed from a given amount of the salt was determined. This method is more rapid than the one previously mentioned, but the results are probably less accurate.

0.3134 gram salt gave 0.5434 gram $AgCl + AgBr$, and 0.3238 gram precipitated 0.40001 gram Ag. Hence $Br = 0.0521$ gram in 0.3134 gram salt $= 16.62$ per cent., and $Cl = 0.1041$ gram in 0.3134 gram salt $= 33.22$ per cent.

III. A complete analysis was made of a deposit intermediate between the two just given:

0.4719 gram lost at 105°–110° 0.0671 gram $H_2O = 14.22$ per cent. H_2O, and gave 0.1564 gram K_2SO_4 (14.88 per cent. K), and 0.1395 gram Mn_3O_4 (21.29 per cent. Mn).

0.3426 gram gave 0.5966 gram $AgBr + AgCl$, and 0.3133 gram precipitated 0.3916 gram Ag. Hence $Br = 14.53$ per cent., and $Cl = 34.62$ per cent. In this case the potassium was weighed as sulphate, to ensure the absence of bromine.

The above analyses show that the substance obtained is not a

definite compound, but, in all probability, an isomorphous mixture of two salts. It was found by calculation that the mixture might consist of 77.2 per cent. $KMnCl_3.2H_2O$ with 22.8 per cent. $KMnBr_3.2H_2O$, or, supposing the mixed salts to exist, of 48.05 per cent. $KMnCl_3.2H_2O$ with 51.95 per cent. $KMnCl_2Br.2H_2O$.

	Calculated for both mixtures.	Found.
Cl	34.73	34.62
Br	14.78	14.53
Mn	21.32	21.29
K	15.19	14.88
H_2O	13.98	~~14.22~~
	100.00	99.54

As the substance comes out of a solution containing a large excess of manganous chloride, as well as some manganous bromide, the agreement between the calculated composition and that found can hardly be expected to be very close. The fact that the salt $KMnBr_3.2H_2O$ was not obtained in the experiments with the pure bromides might be considered as an argument in favor of the belief that the constituent containing bromine in this mixture was really some *mixed* salt, such as $KMnCl_2Br.2H_2O$. However, the explanation that the presence of the salt $KMnCl_3.2H_2O$ gives crystallising power to the salt $KMnBr_3.2H_2O$, so that the two can form an isomorphous mixture, involves perhaps less speculation.

When potassium iodide was used instead of the bromide, in attempting to prepare a mixed salt, crystals of the same habit as before were obtained. A complete analysis of these was made, and the salt was found to contain an amount of iodine so small that it must be considered as a non-essential constituent, present merely by the adhering of a certain amount of mother-liquor. The salt is too easily soluble to admit of its being washed to any considerable extent. In no case was so much as 1 per cent. of iodine found. The salt was, in fact, $KMnCl_3.2H_2O$.

These experiments are of interest as showing what large amounts of potassium bromide and iodide are converted into the chloride by being dissolved in a solution of manganous chloride. These crystallisations were all made in neutral solutions so as to avoid the complications, in interpreting the results, which the presence of even a small quantity of acid would have introduced.

On adding excess of potassium chloride to a warm, saturated solution of manganous bromide in water, filtering while hot, and allowing to cool, a deposit of crystals was obtained consisting largely of potassium bromide. The solution was then evaporated and each successive deposit of crystals removed until a point was at length reached where crystals similar to those of $KMnCl_3.2H_2O$ were formed. They contained bromine and manganese, as well as potassium and chlorine. Analysis showed that they did not correspond in composition to any definite simple salt, but were a mixture (probably an isomorphous mixture) of two or more compounds. It is probable that this substance contained the same salts as that produced by adding potassium bromide to a solution of manganous chloride.

A similar experiment using manganous iodide instead of the bromide gave no satisfactory results, manganous iodide being rather too unstable for this work. It was not to be expected, however, that a double salt would be obtained in this experiment, because the composition of the salts already described seems to prove that both manganous chloride and potassium chloride are necessary constituents in every case. The experiments with manganous chloride and potassium iodide showed how readily the chlorine passed over from the manganese to the potassium, so that it does not seem probable that the reverse action would take place to any considerable extent; hence the solution, in the experiment just mentioned, would contain only a very small quantity of manganous chloride, and the formation of a double salt would not be possible.

Crystallography of the salt.—Accurate measurements of the crystals were found very difficult, owing to the softness of the salt and its tendency towards deliquescence. Sufficient information was obtained, however, from the optical properties and measurements of some angles to show that the crystals are triclinic. Individual crystals often show very irregular development. The drawing given (Fig. 3) is merely to show their general shape, as most commonly obtained. As *gliding* is very readily produced in this salt, a sample of it was sent to Prof. Otto Mügge, of the University of Münster, who has been for some time making a special study of that phenomenon. He has kindly undertaken an investigation of the compound.

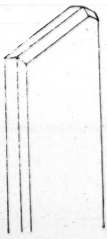


FIG. 3.

Experiments with Ammonium Chloride.

Up to the present time there have been described three compounds of manganous chloride with ammonium chloride:

$NH_4MnCl_3.2H_2O$, described by Hautz;[1]
$(NH_4)_2MnCl_4.H_2O$, described by Rammelsberg[2] and by Pickering;[3]
$(NH_4)_2MnCl_4.2H_2O$, described by v. Hauer.[4]

The directions given by Hautz for the preparation of the salt described by him are simple. A solution of manganous chloride and ammonium chloride, mixed in the proportions required by the formula NH_4MnCl_3, is to be evaporated to crystallisation. These directions being followed, a salt was obtained, which was evidently the same as that described by Hautz. Analysis proved, however, that its formula was not $NH_4MnCl_3.2H_2O$, but $(NH_4)_2MnCl_4.2H_2O$, though the salt as thus produced was not very pure. A pure product was afterwards obtained by mixing the two chlorides in about the proportions mentioned by Hautz, and allowing the aqueous solution to evaporate spontaneously for several months over sulphuric acid. At intervals the deposits of crystals were removed. The fifth sample was found to be pure; the others contained an excess of ammonium chloride.

The analyses of the salt gave the following results:

0.3693 gram gave 0.7870 gram AgCl (52.70 per cent. Cl).

0.3557 gram gave 0.1008 gram Mn_3O_4 (20.41 per cent. Mn).

1.1389 grams lost at 110° 0.1529 gram H_2O = 13.43 per cent. H_2O.

0.3015 gram gave 0.04037 gram NH_4 = 13.39 per cent. NH_4.

The determination of the water of crystallisation in this salt is of no value. The water is not given off readily, and the anhydrous salt undergoes slow decomposition at 110°. The figures given merely indicate, therefore, the point beyond which the loss of weight was very slow.

	Calculated for $(NH_4)_2MnCl_4.2H_2O$.		Found.
Mn	54.80	20.43	20.41
4Cl	141.48	52.75	52.70
$2NH_4$	36.02	13.43	13.39
$2H_2O$	35.92	13.39	13.43
	268.22	100.00	99.93

[1] Ann. Chem. (Liebig) **66**, 285.
[2] Pogg. Ann. **94**, 507.
[3] Jour. Chem. Soc., 1879, 654.
[4] J. prakt. Chem. **63**, 436.

The salt usually forms radiating groups of short crystals. It is pale pink in color and of hard texture. It is easily soluble in water, but cannot be obtained very pure by recrystallisation, as it requires the presence of an excess of manganous chloride before it crystallises in quite pure condition. It is not deliquescent in the air, and does not give up its water of crystallisation in a desiccator.

Crystallography of the salt.—Well-developed, individual crystals are not often obtained, and when found, the faces are not, as a rule, bright enough for a satisfactory measurement of the angles with a goniometer. The salt (Fig. 4) is monoclinic in crystallisation, but possesses certain peculiarities due to the fact that two of its axes are almost (if not exactly) equal in length. While the values obtained for these axes are not identical, the difference is quite within the possible error caused by the imperfections of the crystal faces. Owing to the habit of the crystals and the similarity in length of two of the axes, there is some resemblance between crystals of this salt and a rhombic dodecahedron. The cleavage is imperfect. The optical properties show that the crystals are monoclinic. The position of the *b* axis (the axis of symmetry) was determined by the extinction phenomena of the substance.

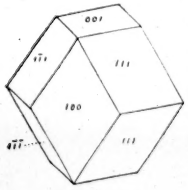


FIG. 4.

The forms observed were oP, ∞ P $\bar{\infty}$, + P and — P.

Measurements obtained.	Angles calculated.
111 : $\bar{1}$11 = 121° 36½′	121° 37′
111 : 11$\bar{1}$ = 90° 16½′	90° 17′
111 : $\bar{1}$1$\bar{1}$ = 95° 42′	95° 42′
111 : 100 = 121° 30′	121° 29½′
111 : 1$\bar{1}$1 = 121° 36½′	121° 48′
111 : 100 = 117° 43′	116° 53½′
001 : 100 = 95° 25′	95° 25′
111 : 001	121° 26½′
$\bar{1}$11 : 001	116° 47½′

These measurements were all made (except the last) from one crystal of the pure salt as used for analysis. The first four measurements were believed to be the best, and were therefore used in

calculating the lengths of the axes, and the angle β. They are probably correct within 5′ or 6′. Those lower on the list were not believed to be as good. The constants found were:

$$\dot{a} = 1.4913 \qquad \bar{b} = 1$$
$$\dot{c} = 1.4956 \qquad \angle\beta = 84° 35'$$

Hautz describes the salt obtained by him as crystallising in the monoclinic system. The symbols he gives for the forms observed appear to mean that the crystals consisted of a prism, ortho and clino domes, with perhaps one of the pinacoids poorly developed. The symbol of the latter is enclosed in a parenthesis, and it is not clear to which pinacoid it refers. Now, by placing the crystals obtained in this investigation in an incorrect position the forms would become the same as those given by Hautz, except that no plane corresponding to his undetermined pinacoid was observed. The evidence is therefore pretty clear that the two salts are identical. The analyses of Hautz show that the substance as obtained by him was very impure, whatever its formula may have been. He describes the salt as losing 1½ molecules of water at 100°, and the remainder at 135°. It has already been pointed out that determinations of the water in this salt are quite unreliable on account of the tendency to decomposition and the difficulty with which the water is driven off at about 110°. The figures given by Hautz are as follows:

	For salt undried.		For salt dried at 100°.	
	Calculated.	Found.	Calculated.	Found.
NH_4	8.32	8.2	9.84	...
Mn	25.90	...	29.54	28.69
Cl	49.12	...	55.76	55.52
H_2O	16.66	17.4	4.86	4.09
	100.00		100.00	

These figures would be somewhat different if calculated on the basis of the atomic weights now in use; but even then the lack of agreement between the numbers calculated and those found by analysis would be too great, in some cases, to be attributed to errors of experiment. From these partial analyses Hautz derives the formula (using our present atomic weights) $NH_4MnCl_3.2H_2O$ for the undried salt, and $NH_4MnCl_3.\frac{1}{2}H_2O$ for the salt dried at 100°.

It was not found possible to prepare this substance. Even when a large excess of manganous chloride was present in the salt,

$(NH_4)_2MnCl_4.2H_2O$ was invariably obtained. From a consideration of all the evidence, the conclusion is drawn that the salt obtained by Hautz was really $(NH_4)_2MnCl_4.2H_2O$ in an impure condition, and that no salt exists having the formula $NH_4MnCl_3.2H_2O$. This conclusion was quite unexpected, as it was naturally supposed that there would be an ammonium salt corresponding to the potassium salt obtained. The relations between all the members of this series of salts will be referred to farther on.

The salt $(NH_4)_2MnCl_4.2H_2O$, as obtained and analysed by v. Hauer, seems to have been quite impure. He describes it as crystallising in cubes of a yellow or pale red color, which became almost white after recrystallisation. This description is entirely erroneous, except in regard to the pale redness of the salt.

The belief in the existence of the salt $(NH_4)_2MnCl_4.H_2O$ rests on the authority of Rammelsberg and of Pickering. The former states that it crystallises in the regular system, and publishes a partial analysis in proof of the formula given by him. His figures are as follows:

	Calculated.	Found.
Mn	21.97	21.03
4Cl	56.52	...
$2NH_4$	14.34	14.08
H_2O	7.17	...
	100.00	

While the figures obtained in the case of ammonium are fairly close to those calculated, it should be observed that in the case of manganese the figures found are about $\frac{3}{10}$ of a unit nearer to the formula with *two* molecules of water of crystallisation, than to that given by Rammelsberg. Pickering obtained a salt crystallising in hard brown cubes, which after recrystallisation from water gave figures, on analysis, which "corresponded perfectly to the formula" $(NH_4)_2MnCl_4.H_2O$. Unfortunately these figures were not published.

In regard to this salt a series of experiments was carried out, the results of which are here given. The samples analysed were obtained under widely differing conditions.

I. Obtained by rapid cooling of a solution containing manganous chloride and ammonium chloride in proper proportions for the formula $(NH_4)_2MnCl_4$.

0.6610 gram gave 0.0985 gram Mn_3O_4 (10.73 per cent. Mn).

0.2733 gram gave 0.6521 gram AgCl (59.00 per cent. Cl).

II. Obtained by spontaneous evaporation of a solution of the mixed chlorides.

0.3703 gram gave 0.0771 gram Mn_3O_4 (15.00 per cent. Mn).

0.3401 gram gave 0.7668 gram AgCl (55.75 per cent. Cl).

III. A solution was evaporated by heat, and crystallisation allowed to take place by slow cooling.

0.5497 gram gave 0.1161 gram Mn_3O_4 (15.21 per cent. Mn).

0.2974 gram gave 0.6666 gram AgCl (55.43 per cent. Cl).

IV. Prepared by the same method.

0.3355 gram gave 0.0892 gram Mn_3O_4 (19.15 per cent. Mn).

0.2298 gram gave 0.4964 gram AgCl (53.42 per cent. Cl).

V. Obtained by the spontaneous evaporation of a solution containing a large excess of manganous chloride.

0.3557 gram gave 0.1008 gram Mn_3O_4 (20.41 per cent. Mn).

0.3693 gram gave 0.7870 gram AgCl (52.70 per cent. Cl).

VI and VII. These are analyses of the precipitate first mentioned by Godeffroy,[1] which is produced when a saturated solution of manganous chloride in concentrated hydrochloric acid is added to a similar solution of ammonium chloride. As this precipitate had not been previously analysed, it was hoped that it might prove to be a definite compound. It is, however, a mixture of varying composition. Of the two samples obtained, the color of the second was much more decidedly pink than that of the first. They were both dried on a porous plate, and then to constant weight over caustic potash.

VI. Precipitated by mixing solutions at ordinary temperatures.

0.3432 gram gave 0.1056 gram Mn_3O_4 (22.19 per cent. Mn).

0.3112 gram gave 0.6572 gram AgCl (52.22 per cent. Cl).

VII. Precipitated by mixing solutions previously cooled to about 0°.

0.3667 gram gave 0.1202 gram Mn_3O_4 (23.61 per cent. Mn).

0.3592 gram gave 0.7367 gram AgCl (50.72 per cent. Cl).

These results form a series in which the percentage of manganese increases and that of chlorine decreases, as here arranged:

[1] Ber. d. chem. Ges. **8**, 9.

	Mn.	Cl.
I.	10.73	59.00
II.	15.00	55.75
III.	15.21	55.43
IV.	19.15	53.42
V.	20.41	52.70
VI.	22.19	52.22
VII.	23.61	50.72

The calculated percentages for the formula $(NH_4)_2MnCl_4.H_2O$, using accurate atomic weights, are Mn 21.90 and Cl 56.53. It is evident that no such salt was obtained. Only one substance in the above list was a definite compound, namely the fifth, already described as the salt $(NH_4)_2MnCl_4.2H_2O$. Its crystalline form was definite. I, II and III formed indefinite masses of ill-defined crystals. VI and VII were amorphous precipitates. IV crystallised, at least in part, in perfectly definite octahedrons. As the analysis showed it to be a mixture, it appears highly probable that the octahedrons consisted of impure ammonium chloride, while the remainder of the deposit contained a large amount of the double salt with *two* molecules of water. This might account for the fact that both Rammelsberg and Pickering state that the salt obtained by them is regular in crystallisation. Pickering obtained cubes. It seems probable that in some of the other specimens recorded in the above list manganous chloride was present as a mechanical admixture. As no definite directions are given for the preparation of the salt described by Rammelsberg and by Pickering, absolute proof of its non-existence can hardly be expected. The investigation above related seems, however, to give sufficient proof. It is to be remembered that the only published analytical evidence which is really in favor of the existence of the salt consists of one determination of the ammonium.

From the results obtained in this work with ammonium chloride, the conclusion is drawn that only one compound of that substance with manganous chloride has ever been found, namely the salt $(NH_4)_2MnCl_4.2H_2O$.

Experiments with Rubidium Chloride.

According to R. Godeffroy,[1] rubidium chloride forms with manganous chloride two compounds, differing, however, only in

[1] Archiv der Pharmacie [3] **12**, 47; Zeitschr. des allg. österreichischen Apotheker-Vereins, 1875, 21.

the amount of water of crystallisation contained in them. One is described as a pale rose-red, crystalline powder, having the composition represented by the formula Rb_2MnCl_4. By recrystallising this precipitate, crystals of the formula $Rb_2MnCl_4.3H_2O$ are said to be obtained. The precipitate was here investigated first. It is obtained by bringing together concentrated solutions of manganous chloride and of rubidium chloride, concentrated hydrochloric acid having been used as the solvent in both cases. The precipitate was prepared several times under slightly different conditions of temperature. In every case it was dried according to the method already described under the experiments with ammonium chloride. On subsequent heating to about 105° in an air-bath, every specimen was found to give up water of crystallisation. Partial analyses of three of the samples are here recorded:

I. 2.6691 grams lost at 105°–110° 0.2395 gram H_2O = 8.97 per cent. H_2O.

II. 0.5120 gram lost at 105°–110° 0.0537 gram H_2O = 10.49 per cent. H_2O.

III. 1.3399 grams lost at 105°–110° 0.1705 gram H_2O = 12.72 per cent. H_2O.

The precipitates thus dried were found to contain varying amounts of chlorine.

I. 0.3464 gram gave 0.5408 gram AgCl (38.61 per cent. Cl).

II. 0.3124 gram gave 0.5066 gram AgCl (40.10 per cent. Cl).

III. 0.3216 gram gave 0.5591 gram AgCl (42.99 per cent. Cl).

If these percentages of chlorine be calculated back so as to represent percentages in the salt *before* the combined water was driven off, they become—

I. 35.15 per cent. Cl.

II. 35.89 per cent. Cl.

III. 37.52 per cent. Cl.

All the precipitates were very pale pink in color, the tint being, however, noticeably darker in the case of the third than in the others.

The figures obtained by Godeffroy are as follows:

	Calculated for Rb_2MnCl_4.	Found.
4Cl	38.71	38.48
Mn	14.95	14.00
2Rb	46 34	45.97
	100.00	98.45

From a consideration of all the above facts the conclusion is drawn that the precipitate produced by mixing concentrated solutions of manganous chloride and rubidium chloride in concentrated hydrochloric acid is not anhydrous and is not a single, definite chemical compound, but a mechanical mixture of variable composition. These conclusions harmonise with those arrived at in studying the similar precipitate produced in the case of ammonium chloride.

When the precipitate is dissolved in water and the solution evaporated, extremely pale, pink crystals are obtained, usually forming radiating groups. This substance Godeffroy found to have the composition represented by the formula $Rb_2MnCl_4.3H_2O$, the salt losing two molecules of water at 100° and the remainder at 150°. After working on this salt for some time it was found that it encloses a considerable amount of water mechanically, which is only given off with extreme slowness in a desiccator, unless the salt has been previously thoroughly powdered. Godeffroy does not mention having taken this precaution, and it therefore seems probable that it was partly owing to the error introduced at this point that his analysis led to the formula with three molecules of water instead of the correct one with only two. At 150° the manganous chloride would become partly oxidised, and thus an additional loss in weight—and an additional error—would be obtained. Godeffroy's figures are here given:

	Calculated for $Rb_2MnCl_4.3H_2O$.	Found.
2Rb	40.53	...
Mn	13.03	13.17
4Cl	33.65	33.83
$2H_2O$	8.76	8.54
H_2O	4.03	3.54
	100.00	

In the present investigation the following figures were obtained, the salt having been dried to constant weight, in powdered condition, over calcium chloride:

0.3589 gram gave 0.5099 gram AgCl (35.13 per cent. Cl), and 0.0677 gram Mn_3O_4 (13.59 per cent. Mn).

0.2856 gram lost at 105°–110° 0.0259 gram $H_2O = 9.07$ per cent. H_2O, and gave 0.1707 gram RbCl (42.24 per cent. Rb).

	Calculated for $Rb_2MnCl_4.2H_2O$.		Found.
2Rb	170.4	42.33	42.24
Mn	54.8	13.61	13.59
4Cl	141.48	35.14	35.13
$2H_2O$	35.92	8.92	9.07
	402.60	100.00	100.03

The composition of the salt, therefore, corresponds to that required by the formula $Rb_2MnCl_4.2H_2O$. It is easily soluble in water and can be recrystallised. It readily loses all its water of crystallisation at 110°. It does not deliquesce in the air, and does not lose its water of crystallisation when placed over calcium chloride. This latter point needs, perhaps, further discussion in consideration of the method used for drying the salt for analysis. In the first place it is to be noted that the salt can be dried in ordinary dry air, provided it is in a finely powdered condition, though the process is more rapid over calcium chloride. That the water given off in this drying is not water of crystallisation is clear from three considerations: 1st. it varies in amount; 2d. on examining a crystal of the salt under a microscope, inclusions of water can be seen; 3d. a crystal does not lose its form or transparency when dried over calcium chloride.

Efforts to obtain a salt corresponding to $KMnCl_3.2H_2O$ were made, but no such rubidium salt was found even when a considerable excess of manganous chloride was present. This investigation shows that, in all probability, the only definite compound of manganous chloride with rubidium chloride which is capable of isolation is the salt $Rb_2MnCl_4.2H_2O$.

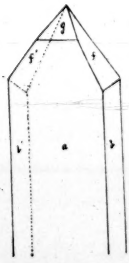


FIG. 5.

Crystallography of the salt.—It is obtained best by spontaneous evaporation of the aqueous solution. The crystals frequently form radiating groups. When well developed they form elongated tabular crystals. In habit they are not always the same, though a common type is that represented in Fig. 5. This consists of two individuals twinned and united along a plane running parallel to the long axis of the crystal. The crystallisation is triclinic, as shown by the optical properties and measurements of the angles. There is no reëntrant angle formed where the two parts of the twin unite, hence the composition face is not a crystal-

lographic plane. The substance shows gliding phenomena. Its crystallography was not worked out in full. The measurements made are, however, pretty accurate, and it is believed that they, together with the rough drawing, will be sufficient for the satisfactory identification of the salt at any time. The cleavage is well marked parallel to the plane *b*.

The following values were obtained by measurement:

$a : b = 84° 57'$.
$a : b' = 95° 5'$.
$a : f = 104° 41'$.
$a : f' = 75° 16'$.
$f : f_1$ (over summit) $= 70° 36\frac{1}{2}'$.
$a : g = 169° 27'$.
$b : f = b' : f' = 138° 40\frac{1}{2}'$ or $141° 42'$. The presence of vicinal planes made the true value of this angle uncertain. The plane *g* does not occur on the other side of the crystal at the same end. Good doubly-terminated crystals were not obtained.

Experiments with Cæsium Chloride.

In the papers already referred to, Godeffroy claims to have found three distinct compounds of manganous chloride with cæsium chloride, namely, a precipitate Cs_2MnCl_4 and two crystalline salts $Cs_2MnCl_4.3H_2O$ and $2(Cs_2MnCl_4).5H_2O$. The precipitate is obtained under the same conditions as were mentioned in the case of ammonium chloride. The substance was prepared three times in slightly different ways, and a partial analysis was made in each case. On drying the precipitate, as in the previous experiments, over caustic potash, a constant weight was not obtained even after a period of two weeks. It is evident that this loss was due to the slow abstraction of water of crystallisation. The determinations of the combined water are necessarily approximate only. The salt was dried first on a porous plate, and then for a few hours over caustic potash before the determination was made

I. Solutions slightly warmed at the time of precipitation:

0.6935 gram lost at 105°–110° 0.0804 gram $H_2O = 11.59$ per cent. H_2O.

After thus drying, 0.3116 gram gave 0.0805 gram Mn_3O_4 (18.61 per cent. Mn), and 0.3001 gram gave 0.4375 gram AgCl (36.05 per cent. Cl).

II. Solutions cooled to about 0° at the time of precipitation:

0.8523 gram lost at 105°–110° 0.0922 gram H_2O = 10.82 per cent. H_2O.

After thus drying, 0.3242 gram gave 0.0843 gram Mn_2O_4 (18.73 per cent. Mn), and 0.03416 gram gave 0.4991 gram AgCl (36.13 per cent. Cl).

III. The solution of manganous chloride was quite dilute, the acid in which it was dissolved being, as before, concentrated.

1.1491 grams lost at 105°–110° 0.1189 gram H_2O = 10.35 per cent. H_2O.

After thus drying, 0.3589 gram gave 0.0925 gram Mn_2O_4 (18.56 per cent. Mn), and 0.3032 gram gave 0.4432 gram AgCl (36.15 per cent. Cl).

	Calculated for $CsMnCl_3.2H_2O$.	Found.		Calculated for $CsMnCl_3$.	Found.
$2H_2O$	10 90	11.59	Mn	18.66	18.61
		10.82			18.73
		10.35			18.56
			3Cl	36.14	36.05
					36.13
					36.15

The precipitate consists therefore of the salt $CsMnCl_3.2H_2O$ in almost pure condition. After drying in an air-bath at 105° its composition corresponds to the formula $CsMnCl_3$. No compound of cæsium chloride with manganous chloride in these proportions has hitherto been described. The results which Godeffroy obtained by analysis of the precipitate, prepared in the same way as the above, are:

	Calculated for Cs_2MnCl_4.	Found.
2Cs	57.47	57.76
Mn	11.87	11.11
4Cl	30.66	31.04
	100.00	99.91

He seems to have analysed the salt only once. He does not state the manner in which the precipitate was dried. No explanation is here offered to account for the disagreement between these results and those obtained in the present investigation, but the author feels compelled to conclude that there was some serious error in the work of Godeffroy.

The pale pink precipitate just described is easily soluble in water. When the solution is evaporated, crystals are obtained

belonging to the orthorhombic system. These can be recrystallised and are then found to be in pure condition. The salt is pale pink in color. It is not deliquescent in the air under ordinary conditions; but, when powdered, it loses its water of crystallisation in a good desiccator over calcium chloride. This loss, which is very slow, has already been referred to in the case of the impure, precipitated salt. It gives up its water of crystallisation very readily at 105°. For analysis the salt was dried by pressure between layers of filtering paper.

0.5028 gram lost at 105° 0.0548 gram H_2O = 10.90 per cent. H_2O. The dried salt was then analysed.

0.4212 gram gave 0.1092 gram Mn_2O_4 (18.67 per cent. Mn), and 0.2416 gram CsCl (45.29 per cent. Cs).

0.4480 gram gave 0.6547 gram AgCl (36.14 per cent. Cl).

	Calculated for $CsMnCl_3.2H_2O$.		Found.
$2H_2O$	10.90		10.90
	Calculated for $CsMnCl_3$.		Found.
Cs	132.7	45.20	45.29
Mn	54.8	18.66	18.67
3Cl	106.11	36.14	36.14
	293.61	100.00	100.10

The crystallised salt has therefore the formula $CsMnCl_3.2H_2O$, and loses all of its water at 105°.

Crystallography of the salt.—The substance forms tabular crystals, which are shown by their optical properties and angular measurements to be orthorhombic (Fig. 6). The forms observed were, oP, $\infty P\bar{\infty}$, $\infty P\breve{\infty}$, ∞P and $P\bar{2}$. The reflections obtained in the goniometer were not, as a rule, very good, and the exact values of the angles are rendered additionally doubtful in some cases, owing to the presence of vicinal planes.

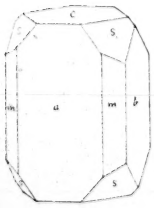


FIG. 6.

$c = oP$, [001].
$a = \infty P\bar{\infty}$, [100].
$b = \infty P\breve{\infty}$, [010].
$m = \infty P$, [110].
$s = P\bar{2}$, [122].

By comparing together many measurements the following

values were obtained, which appeared sufficiently trustworthy for the determination of the axial ratios:

$s : a = 116° 14'$.
$s : c = 124° 7'$.
$s : s = 127° 32'$.
$m : b = 128° 6'$.
$m : a = 141° 54'$.

The axial ratios deduced are $a = .7919$, $b = 1$, $c = 1.2482$.

When the angles given above are calculated from these axial ratios they become:

$s : a = 116° 14'$.
$s : c = 124° 7'$.
$s : s = 127° 32'$.
$m : b = 128° 22\frac{1}{2}'$.
$m : a = 141° 37\frac{1}{2}'$.

The cleavage is parallel to *a*.

If cæsium chloride be added to a solution of the salt $CsMnCl_3 . 2H_2O$, crystals are deposited, on evaporation, which are quite different in habit from those previously obtained, and are much paler in color. These proved to be the salt corresponding to that obtained when working with rubidium chloride, having the formula $Cs_2MnCl_4 . 2H_2O$. This is probably the compound obtained by Godeffroy and regarded by him as two different salts, namely $Cs_2MnCl_4 . 3H_2O$ when crystallised out of an aqueous solution, and $2(Cs_2MnCl_4) . 5H_2O$ when crystallised out of a solution in concentrated hydrochloric acid. The salt is not deliquescent in ordinary air, and retains its water of crystallisation when dried in an ordinary desiccator. For analysis it was dried, in the form of a fine powder, over calcium chloride. Its water of crystallisation is readily driven off at 105°.

0.4311 gram gave 0.0663 gram Mn_2O_4 (11.08 per cent Mn), and 0.2923 gram CsCl (53.53 per cent. Cs).

0.2204 gram lost at 105° 0.0162 gram $H_2O = 7.35$ per cent. H_2O, and gave 0.2532 gram AgCl (28.41 per cent. Cl).

	Calculated for $Cs_2MnCl_4 . 2H_2O$.		Found.
2Cs	265.4	53.34	53.53
Mn	54.8	11.01	11.08
4Cl	141.48	28.43	28.41
$2H_2O$	35.92	7.22	7.35
	497.60	100.00	100.37

The salt corresponds in composition to the formula $Cs_2MnCl_4.2H_2O$. Godeffroy's analyses of this salt, which seemed to indicate the presence of three molecules of water, were no doubt vitiated by the incomplete drying of the salt before analysis, as was pointed out in the case of the corresponding rubidium compound. His figures are:

	Calculated for $Cs_2MnCl_4.3H_2O$.	Found.
2Cs	51.39	...
Mn	10.65	10.07
4Cl	27.50	27.24
$3H_2O$	10.46	10.96 and 10.23
	100.00	

No evidence was found in favor of the existence of a salt of this composition.

Crystallography of the salt $Cs_2MnCl_4.2H_2O$.—This was not worked out in full, but the following details are given to serve for the identification of the substance. It is triclinic in crystallisation, resembling, in general appearance, the corresponding rubidium salt. The cleavage is, however, parallel to the best developed face, *a*, which is not true of the rubidium compound. Another difference between the two salts is observed in regard to the method of twinning. The cæsium salt shows a reëntrant angle of about 169° where the two individuals are joined, while the rubidium salt does not. Other differences are evident from the measurements. Fig. 7 gives a rough drawing of a crystal of this salt, not twinned. Most of the measurements here given are the mean of two, made on different crystals. They generally agreed within a few minutes. The last two are only approximate. The plane *g* occurs only on one side of the crystal at each end.

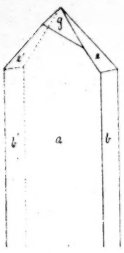


FIG. 7.

The following measurements were obtained:

$a : b = 95° 27'$ (hence $a : b' = 84° 33'$).
$a : g = 139° 24'$.
$b : e = 151° 6'$.
$b' : e' = 154° 1\frac{1}{2}'$.
$e : e'$ (over summit) $= 54° 53\frac{1}{2}'$.
$a : e = 85\frac{3}{4}°$.
$a : e' = 97\frac{1}{4}°$.

A careful attempt was made to prepare the salt $2(Cs_2MnCl_4).5H_2O$ by following the directions of Godeffroy as closely as possible. The solution in concentrated hydrochloric acid, which remained over the precipitate of slightly impure $CsMnCl_3.2H_2O$, was evaporated without the aid of heat, by drawing a stream of dry air over it for several months. A few small crystals were at length obtained. These were very pale pink in color and seemed to be the salt $Cs_2MnCl_4.2H_2O$. On attempting to isolate the compound, after further evaporation of the solution, it was found that some other substance, probably manganous chloride, had crystallised out as well. As it was evidently impossible to obtain a pure product without recrystallisation, which would have been to depart from the conditions mentioned by Godeffroy, the subject was not followed up. In view of the existence of the salt $Cs_2MnCl_4.2H_2O$, and of the non-existence of the salt $Cs_2MnCl_4.3H_2O$ described by Godeffroy, and in view of the weak evidence brought forward to prove the existence of the salt $2(Cs_2MnCl_4).5H_2O$, the matter did not seem worthy of further investigation. The existence of the salt under consideration seems in the highest degree improbable.

Experiments with Magnesium Chloride and with Magnesium Bromide.

In this part of the work it was found more satisfactory to use alcohol and water, instead of water alone, as a solvent. Seventy per cent. of alcohol is probably about the best strength. The solutions were always kept acidified to prevent the decomposition of the magnesium salt. When a solution of manganous chloride and magnesium chloride is evaporated the two chlorides unite, forming one or, perhaps, more compounds, the appearance of which varies greatly according to the exact conditions of formation. Many experiments were performed. In general a compound was obtained crystallising in flattened, sometimes feather-like crystals, which were never found to be pure. On one occasion these plates were left standing for several weeks in contact with the mother-liquor, and were found to be entirely transformed into crystals almost round in shape, usually about $\frac{1}{2}$ cm. in diameter. They could not be investigated crystallographically, owing to their rapid deliquescence. Though not obtained in pure condition, analysis shows that this salt corresponds in composition to the bromide, described below, which is much more easily worked

with. The flattened crystals of the chloride seem to have the same composition as the rounded ones, though they were never obtained in a condition approaching purity. As this double chloride, in whatever form it is obtained, is deliquescent in the air and loses some of its water of crystallisation over calcium chloride, a satisfactory analysis of it could not be made. It was dried for a few hours in a desiccator, but was found when analysed to contain, still, a considerable amount of hygroscopic water. For the method of analysis see below.

0.7608 gram gave 0.1981 gram Mn_3O_4 (18.76 per cent. Mn), and 0.1569 gram $Mg_2P_2O_7$ (4.50 per cent. Mg).

0.9970 gram gave 1.4961 grams AgCl (37.11 per cent. Cl).

The water of crystallisation is not all given off without decomposition of the salt.

	Calculated for $Mn_2MgCl_6.12H_2O$.		Found.
2Mn	109.6	19.52	18.76
Mg	24.21	4.31	4.50
6Cl	212.22	37.79	37.11
$12H_2O$	215.52	38.38	...
	561.55	100.00	

If we allow for the hygroscopic water, which seems to be present, 1½ per cent., we obtain Mn 19.15, Mg 4.59 and Cl 37.88 per cent. The salt, though somewhat impure, evidently corresponds in composition to the bromide mentioned below, and has the formula $Mn_2MgCl_6.12H_2O$.

As noticed near the commencement of this paper, when a large excess of manganous chloride is present the salt $Mn_2Cl.2H_2O$ is produced. No evidence was found of the existence of a salt containing manganous chloride and magnesium chloride in the proportions of one molecule to one.

When manganous bromide and magnesium bromide are present in a solution in the proportion of two molecules of the former to one of the latter, and the solution is evaporated, a double salt crystallises out on cooling. The substance usually forms a compact mass of red crystals at the bottom of the beaker. It can be recrystallised, but well-formed, individual crystals are seldom obtained. It is deliquescent in the air. No loss of water of crystallisation was observed when it was dried over calcium chloride. The most convenient method found for the separation

of the metals, in analysis, was as follows: Decompose the salt with a small amount of sulphuric acid, and heat till all the hydrochloric (or hydrobromic) acid is driven off; then add a solution of ammonium chloride, and heat nearly to boiling. Add gradually ammonium sulphide free from carbonate. Keep hot for about an hour, and then filter and wash. The manganous sulphide is then dissolved in dilute hydrochloric acid, filtered free from sulphur, and precipitated as carbonate after driving off the hydrogen sulphide. The solution containing the magnesium is evaporated, acidified, filtered from sulphur, and the magnesium then precipitated in the usual way.

The water of crystallisation present in this salt cannot be determined directly on account of the decomposition of the substance. That decomposition actually takes place before all the water is given off is evident from the darkening in color, and the fact that part of the salt is rendered insoluble in water. The substance was obtained in almost pure condition without recrystallisation, as shown by the following figures obtained:

0.6679 gram gave 0.1235 gram Mn_3O_4 (13.32 per cent. Mn), and 0.0915 gram $Mg_2P_2O_7$ (2.99 per cent. Mg).

0.6654 gram gave 0.8998 gram AgBr (57.55 per cent. Br).

After heating the salt for several hours not far above 100°, and then for seven hours at about 150°, the loss in weight represented 16.27 per cent. of water. Considerable decomposition had taken place.

	Calculated for $Mn_2MgBr_6.12H_2O$.		Found.
2Mn	109.6	13.24	13.32
Mg	24.21	2.93	2.99
6Br	478.56	57.80	57.55
$12H_2O$	215.52	26.03	...
	827.89	100.00	

The formula of the salt is therefore $Mn_2MgBr_6.12H_2O$, corresponding to that of the impure chloride obtained.

Negative Results.

No compound of lithium chloride with manganous chloride was found, but it is worthy of note that the aqueous solution of the mixed chlorides has, when concentrated, a *green* color, which becomes quite brilliant when the solution is heated. When potas-

sium chloride is present instead of lithium chloride, the hot solution appears greenish-brown.

Some evidence of the formation of a compound of sodium chloride with manganous chloride was obtained, but it was not found possible to isolate the product in sufficiently pure condition for analysis, owing to the very great excess of manganous chloride present.

Unsuccessful attempts were made to obtain compounds of manganous chloride with the chlorides of copper (cuprous and cupric), calcium, strontium and barium. A concentrated solution of the mixed chlorides of calcium and manganese possesses a green color, somewhat like that observed in the case of lithium chloride. An almost amorphous mass was obtained, containing manganous chloride and calcium chloride, which may have been an impure double salt, but it was not in a fit condition for analysis.

Conclusion.

The work was not continued beyond magnesium. Compounds have, however, been described of manganous chloride with cadmium chloride[1] and with mercuric chloride.[2] We find, then, that manganous chloride combines with the chlorides of potassium, rubidium and cæsium; but that, following the families according to the periodic system, there is, after cæsium, a gap of considerable length, including chiefly the chlorides of calcium, strontium and barium. Manganous chloride appears incapable of combining with any of the chlorides between cæsium and magnesium. The latter, however, marks the commencement of a new series, with every member of which manganous chloride can probably combine. The explanation of these facts is simple if we assume that the acidic and basic powers of manganous chloride are about equal to those of strontium chloride, and that in its compounds with the chlorides of potassium, rubidium and cæsium, manganous chloride acts in its acidic capacity, while in its compounds with the chlorides of magnesium (zinc?), cadmium, etc., it acts in its basic capacity. Taking this view we should expect a break to occur between these two series.

The compounds hitherto described are given in tabular form at the commencement of the paper. A comparison between that list and the one given below, of the compounds actually found to

[1] v. Hauer, J. prakt. Chem. **68**, 393. [2] v. Bonsdorff, Pogg. Ann. **17**, 247.

exist, will show that the regularity in the series is much greater than was to be supposed.

$KMnCl_3.2H_2O$ (tricl.)	———
———	$(NH_4)_2MnCl_4.2H_2O$ (monocl.)
———	$Rb_2MnCl_4.2H_2O$ (tricl.)
$CsMnCl_3.2H_2O$ (orthorh.)	$Cs_2MnCl_4.2H_2O$ (tricl.)

$Mn_2MgCl_6.12H_2O$.

$Mn_2MgBr_6.12H_2O$.

It will be noticed that these salts are very irregular from a crystallographic point of view. It is strange that two gaps should occur in the left-hand series. Special efforts were made to obtain both of the missing compounds, but without success. Perhaps the entire dissimilarity in crystal system and habit between the potassium and the cæsium salt may be taken as evidence that, though chemically analogous, the two compounds are not really very closely related to each other.

IV.—On Some Double Halides of Antimony.[1]

By Charles E. Saunders.

Since two double chlorides containing antimony had been described by Godeffroy as containing six molecules of alkali chloride to one of antimony chloride, and were therefore to be regarded as exceptions to the general rule governing the composition of the double halides, it was thought best to repeat the work of Godeffroy. The exceptional salts referred to are

$SbCl_3.6CsCl$ and $SbCl_3.6RbCl$.

Experiments with Cæsium Chloride.

It is necessary, first of all, to give a brief review of the work of Godeffroy on this subject. In 1874[2] he published the first statements in regard to the precipitate obtained by mixing solutions of antimony chloride and cæsium chloride in concentrated hydrochloric acid. This precipitate was recrystallised several times and analysed. The mean of five analyses gave him the following

[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1891.

[2] Zeitschr. des allg. österr. Apotheker-Vereins, 1874, 161.

results:[1] Chlorine, 33.419 per cent.; antimony, 30.531 per cent. From these figures he derives the formula $SbCl_3.CsCl$. The numbers calculated from the formula are: Chlorine, 35.93 per cent.; antimony, 30.37 per cent. Godeffroy regarded the precipitate and the crystalline salt as identical in composition, but gives no definite proof in support of this idea. In the year following[2] he published a complete analysis of the salt, assigning to it an entirely new formula, namely, $SbCl_3.6CsCl$. The results he gives are as follows:

Calculated for $SbCl_3.6CsCl$.		Found.
9Cl	25.77	25.68
Sb	9.83	9.40
6Cs	64.40	63.98
	100.00	99.06

While the figures found agree fairly well with those calculated, the fact must not be lost sight of that there is a discrepancy between the figures found in 1874 and those found in 1875 of over seven units in the case of chlorine and of over twenty-one units in the case of antimony. As no explanation of this difference is given, it seems necessary to attribute it to experimental errors in analysis. The methods used in the latter investigation are worthy of notice in this connection. The salt was dissolved in water acidified with tartaric acid, and after precipitation of the chlorine as silver chloride, the antimony was precipitated as sulphide. The sulphide was then oxidised with nitric acid, and the sulphuric acid thus obtained was estimated in the usual way. The amount of antimony was then calculated from the amount of barium sulphate obtained.

In the present investigation the precipitate was prepared in the manner described, the conditions of temperature being, however, slightly varied in the different experiments. The antimony chloride used for the first was purified by precipitation as oxychloride, that for the second by distillation. The precipitate of the double salt is very pale yellow in color. This does not appear to be due to impurities. The crystallised salt has the same color. The precipitates were dried for analysis in the manner before described. The methods of analysis will be referred to later on in the paper.

[1] Ber. d. chem. Ges. 7, 375.

[2] Zeitschr. des allg. österr. Apotheker-Vereins, 1875, 21.

I. 0.6051 gram gave 0.2146 gram Sb_2S_3 (25.32 per cent. Sb), and 0.3162 gram CsCl (41.26 per cent. Cs).

II. 0.7470 gram gave 0.2682 gram Sb_2S_3 (25.63 per cent. Sb), and 0.3880 gram CsCl (41.01 per cent. Cs).

A third preparation of the precipitate, using the same redistilled antimony chloride as was used for the second, gave 25.38 per cent. of antimony. The composition of the precipitate appears therefore to be nearly constant. The figures obtained correspond pretty closely to those required for a salt of the formula $2SbCl_3.3CsCl$.

	Calculated for $Cs_3Sb_2Cl_9$.	Found.	
Sb	25.03	25.32	25.63
Cs	41.66	41.26	41.01

This precipitate is soluble in hot dilute hydrochloric acid, though only slightly soluble in the cold. On evaporation, crystals of various habits are obtained according to the conditions. They generally appear as needles or thin prisms when deposited by the cooling of a hot solution; while by spontaneous evaporation they form thicker prisms or irregular plates, having a rough pseudo-hexagonal appearance produced by twinning. Two or three different samples of the crystallised salt were analysed. The composition of all of them agreed with the formula proposed:

0.3112 gram gave 0.1641 gram CsCl (41.63 per cent. Cs).

0.1940 gram gave 0.0684 gram Sb_2S_3 (25.16 per cent. Sb).

0.2059 gram gave 0 2770 gram AgCl (33.27 per cent. Cl).

0.4237 gram gave 0.1499 gram Sb_2S_3 (25.25 per cent. Sb), and 0.2240 gram CsCl (41.74 per cent. Cs).

0.2203 gram gave 0.2938 gram AgCl (32 97 per cent. Cl).

	Calculated for $Cs_3Sb_2Cl_9$.		Found.	
3Cs	398.1	41.66	41.63	41.74
2Sb	239.2	25.03	25.16	25.25
9Cl	318.33	33.31	33.27	32.97
	955.63	100.00	100.06	99.96

As this salt was obtained with the greatest ease and according to the method described by Godeffroy, the author feels justified in drawing the conclusion that this is the compound for which Godeffroy proposed the formula $SbCl_3.CsCl$ and, later, $SbCl_3.6CsCl$, the correct formula being $Cs_3Sb_2Cl_9$. This salt is therefore no longer to be considered as an exception to the general rule

regarding the composition of the double halides. This is the only compound of cæsium chloride and antimony chloride which is easily obtained. It may be that a salt of the formula $CsSbCl_4$ could be produced under suitable conditions, but the salt above described was the only one identified in the present investigation, though efforts were made to obtain others.

The crystallography of this salt was not worked out. A few details were, however, obtained. It usually crystallises in elongated prisms. These belong to the orthorhombic system, but are sometimes twinned, when very short, in such a way as to give a rough pseudo-hexagonal form. Such a twin is represented in Fig. 8. The three individuals combined in the crystal can be distinguished by examination in parallel polarised light.

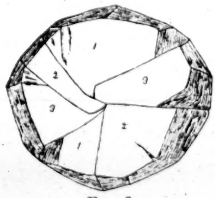


FIG. 8.

Experiments with Rubidium Chloride.

By evaporation of a dilute hydrochloric acid solution containing antimony chloride and rubidium chloride, Godeffroy[1] obtained tabular crystals of a double salt, to which he gave the formula $SbCl_3.6RbCl$. This was analysed by the same method as that described under cæsium chloride. The following are the figures given by Godeffroy:

	Calculated for $SbCl_3.6RbCl$.	Found.
9Cl	33·47	33·45
Sb	12.79	13.10
6Rb	53·74	53.06
	100.00	99.61

A substance corresponding to Godeffroy's description was easily obtained by following his directions, and crystallised out of the solution in dilute hydrochloric acid in beautiful, colorless, six-sided plates, tables, or thicker crystals, according to the conditions. The salt has a very strong crystallising force. It is readily soluble in dilute hydrochloric acid, but less so in the concentrated acid.

[1] Zeitschr. des allg. österr. Apotheker-Vereins, 1875, 21.

By mixing concentrated solutions of rubidium chloride and of antimony chloride in concentrated hydrochloric acid, the double salt is formed as a distinctly crystalline precipitate. Repeated analyses show that the composition of this salt does not correspond to the formula proposed by Godeffroy. The substance was prepared under varying conditions, being crystallised out either by slow cooling of the solution, or by sudden cooling, or by spontaneous evaporation. In the first experiment the two chlorides were mixed in the proportions required by the formula of Godeffroy. In the other cases no special care was taken in regard to the proportions. The composition of the salt formed did not vary appreciably. All the analyses made, in this part of the investigation, are here given, except one attempt to determine rubidium as nitrate, which was quite untrustworthy. The variations from the normal composition are no doubt due to experimental errors, or to the presence of slight impurities in some specimens of the salt.

I. 0.5720 gram gave 0.1902 gram Sb_2S_3 (23.73 per cent. Sb), and 0.8538 gram AgCl (36.91 per cent. Cl).

II. 0.4174 gram gave 0.1401 gram Sb_2S_3 (23.96 per cent. Sb), and 0.2297 gram RbCl (38.89 per cent. Rb).

0.3190 gram gave 0.4772 gram AgCl (36.99 per cent. Cl).

III. 0.4028 gram gave 0.1348 gram Sb_2S_3 (23.89 per cent. Sb), and 0.6007 gram AgCl (36.88 per cent. Cl).

0.6881 gram gave 0.3769 gram RbCl (38.71 per cent. Rb).

IV. 0.2728 gram gave 0.4071 gram AgCl (36.90 per cent. Cl).

V. 0.3359 gram gave 0.1125 gram Sb_2S_3 (23.90 per cent. Sb), and 0.1850 gram RbCl (38.92 per cent. Rb).

A tabular view of these results will make the matter clearer.

	Calculated[1] for $SbCl_3.6RbCl$.	Found by Godeffroy.	Found by the Author.			
			I.	II.	III.	IV. and V.
Sb	12.60	13.10	23.73	23.96	23.89	23.90
6Rb	53.86	53.06	...	38.89	38.71	38.92
9Cl	33.54	33.45	36.91	36.99	36.88	36.90

These figures show that the salt obtained in the present investigation is a definite chemical compound, which does not correspond in composition to the numbers calculated from Godeffroy's formula. That this salt is really identical with that obtained by

[1] These figures differ slightly from those calculated by Godeffroy, owing to the use of different atomic weights in the two cases.

Godeffroy, in spite of the great difference between the analytical results in the two cases, is proved by several considerations. This salt is obtained with the greatest ease, much more readily than any other compound of rubidium chloride with antimony chloride. Of the three salts found this one contains the largest percentage of rubidium, and therefore approaches more nearly than either of the others to the composition required by Godeffroy's formula. The directions of Godeffroy were followed closely in preparing the salt, and in one case at least the two chlorides were present in solution in the proportions required by the above formula. The salt was examined crystallographically by Streng.[1] He describes it as forming hexagonal tables by a combination of the basal plane and fundamental pyramid, with a very slight development of the fundamental prism. In the present investigation no distinct development of the prism was observed. The pyramid faces were strongly striated in a horizonal direction, so that accurate measurements were impossible. The mean of three measurements of P : P over a middle edge gave him 129° 30′, from which he calculated the axial ratio $a:c$ as 1 : 1.836. The crystals obtained in the present investigation agree with the description of Streng. The angle measured by him was here found to vary between 127° and 131°, though the striations on the crystals prevented anything but the roughest measurements. Stauroscopic examination shows that the crystals are not really hexagonal in crystallisation; but as Streng does not seem to have examined his crystals optically, this disagreement in regard to the crystal system cannot be considered as evidence in favor of the two salts being different. The substance as prepared in this investigation was, to all outward appearance, hexagonal in crystallisation, and agreed exactly, except in the points mentioned, with the descriptions given by Godeffroy and by Streng. There can therefore be little doubt that the substances as obtained in the two investigations were identical. The conclusion is therefore drawn that no salt exists having the formula $SbCl_3.6RbCl$.

As the five partial analyses already given showed that the formula of the salt was by no means simple, the matter was taken up again, with a view to obtaining a quantity of the salt in as pure a condition as possible, and then making several analyses. Having prepared a considerable amount of the substance, it was

[1] Archiv der Pharmacie [3] 9, 343.

recrystallised five times from dilute hydrochloric acid. In the last two crystallisations the solution was cooled rapidly, so that the salt was deposited in very small, six-sided scales, possessing a beautiful, pure white, lustrous appearance. The final drying of the compound was as follows: It was first of all dried by pressure between layers of filtering paper previously washed with hydrochloric acid, and was then finely powdered and placed on a watch-glass in a desiccator over phosphorus pentoxide. It was weighed from day to day until the loss in twenty-four hours was not perceptible, the weighings being made to the tenth of a milligram. In this way over two grams of the salt were obtained. The methods of analysis used are now to be described. In nearly all the analyses of salts containing antimony, the methods used were essentially the same as those here given.

The salt was dissolved in dilute hydrochloric acid in an Erlenmeyer flask and the solution heated to incipient boiling. Carefully washed hydrogen sulphide was then passed in until the solution was nearly cold. The flask was then tightly closed and left for at least an hour, when it was heated again to about 60°. The antimony sulphide was collected in a Gooch crucible, the filtration being performed while the liquid was hot. The precipitate was then washed with freshly prepared hydrogen sulphide water and afterward dried for about an hour at 105°. The crucible was then placed in a small air-bath filled with carbon dioxide, into which a current of the washed and dried gas was kept passing. The temperature of this bath was slowly raised to 200° and the flame then extinguished. The sulphide of antimony obtained in this way was black and anhydrous. It was found that all the water can be driven off from the sulphide without converting it into the black form, but the process is very slow. When the black sulphide was heated to 200°–220° for a few hours a slight loss in weight was observed in almost all cases. This may have been due to the decomposition of a minute quantity of oxychloride of antimony present. One precipitation of the sulphide (the fourth) was made after adding a small quantity of tartaric acid to the solution. The precipitate formed in this case also suffered a very slight loss in weight on continued heating. If the presence of oxychloride of antimony be the cause of this reduction in weight it proves that, under the conditions mentioned, excess of hydrogen sulphide does not entirely decompose oxychloride of antimony, even when

acting for so long a time as three hours on the precipitate, the solution being kept warm during one hour. The first weighing of the precipitate was the one assumed to be correct in every case. The subsequent loss in weight was so slight (usually about one-tenth of a milligram in half an hour's heating at 210°), that no great error can have been introduced by neglecting it, whatever may have been its actual cause. The use of carbon dioxide to prevent the presence of oxygen in the solution during or after the precipitation of the antimony sulphide, seems to be quite unnecessary if the above directions be followed.

The rubidium was determined as chloride by evaporation of the filtrate, in which it was contained, in a platinum vessel. Before weighing, it was dried at about 230° and finally heated for a few moments to incipient redness. Special experiments showed that about one-tenth of a milligram of rubidium chloride was lost in the final heating. A correction was therefore made for that loss. The amount of solid matter obtained by the action of the hot solution on the glass during the precipitation of the antimony was determined by a blank experiment under the same conditions. A correction for this gain in weight was introduced in each determination of rubidium.

Chlorine was usually determined by precipitation as silver chloride in a solution of the salt in water acidified with tartaric and nitric acids. The silver chloride was afterwards dissolved in ammonia and reprecipitated. Determination of the chlorine after precipitation of the antimony as sulphide was found extremely difficult. The presence of an excess of free hydrochloric acid seems necessary to bring the antimony sulphide into a condition suitable for filtration.

As the determination of the atomic ratio between antimony and rubidium seemed to promise to give results containing the slightest errors, special stress was laid, in the following analyses, on that ratio. The analyses of the salt gave these results:

I. 0.3844 gram gave 0.1288 gram Sb_2S_3 (23.915 per cent. Sb), and 0.2129 gram RbCl (39.137 per cent. Rb).

II. 0.4401 gram gave 0.1476 gram Sb_2S_3 (23.937 per cent. Sb), and 0.2436 gram RbCl (39.113 per cent. Rb).

III. 0.3936 gram gave 0.1316 gram Sb_2S_3 (23.864 per cent. Sb), and 0.2175 gram RbCl (39.049 per cent. Rb).

IV. 0.3867 gram gave 0.1297 gram Sb_2S_3 (23.939 per cent. Sb).

V. 0.4078 gram gave 0.6115 gram AgCl (37.08 per cent. Cl).

The atomic ratios of antimony to rubidium as deduced from the three analyses are:

I. Sb : Rb as 1 : 2.297.
II. Sb : Rb as 1 : 2.294.
III. Sb : Rb as 1 : 2.297.
Mean Sb : Rb as 1 : 2.296.

From this the following ratios are derived. They are the only ones, at all simple, in which the figures are approximately whole numbers:

Sb : Rb as 4 : 9.184
Sb : Rb as 7 : 16.072
Sb : Rb as 10 : 22.960

The simplest of these ratios, 4 to 9, must be rejected, as the experimental errors due to impurities in the salt or to defects in the analytical methods can hardly have been as great as those which would be indicated by the formula $4SbCl_3.9RbCl$. The figures calculated from the ratios 7 to 16 and 10 to 23 are given below, together with the analytical results obtained by taking the mean of the determinations made with this last sample of the salt. That these results are uniformly higher than those found in the former analyses is probably due to imperfect drying of the salt in the earlier samples. The atomic weights used are Sb 119.6, Rb 85.2, Cl 35.37.

	Calculated for $7SbCl_3.16RbCl$.	Calculated for $10SbCl_3.23RbCl$.	Found.
Sb	23.86	23.776	23.91
Rb	38.85	38.957	39.10
Cl	37.29	37.267	37.08
	100.00	100.000	100.09

It will be seen that the agreement between the calculated composition and that found is closer for the larger formula than for the smaller. Assuming the larger formula to be correct, the disagreement between the figures may be due to errors in analysis, impurities present in the salt, and also perhaps to inaccuracy in the atomic weights used. While it is evidently impossible from these figures to establish the formula of this compound on a firm basis, the analyses prove that the salt is unusually complex in composition, and indicate that the most probable formula is $Sb_{10}Rb_{23}Cl_{83}$.

The salt is extremely stable in some respects. Though easily decomposed by water, as would be expected, it can be heated in an air-bath to a very high temperature without undergoing any appreciable change. At 230° (several degrees above the boiling-point of antimony chloride) it was found to suffer slow decomposition, with loss of weight.

Stauroscopic examination of the salt shows that it is only *pseudo*-hexagonal, being in reality optically biaxial and positive. The acute bisectrix is almost (perhaps quite) normal to the basal plane. The optical behavior of the substance seems to indicate that it is usually composed of a series of superposed plates, with the planes of their optic axes not coincident. In some cases the crystals do not become dark in any position when rotated between crossed nicols. Thinner plates sometimes show an interference figure similar to that produced by two superposed plates of muscovite, with the planes of their optic axes at right angles. The thinnest plates show sharp extinction, and give an interference figure which apparently denotes orthorhombic symmetry. Other plates show a sort of extinction wave or brush, which traverses the crystal when it is rotated between crossed nicols in parallel polarised light. Owing to the striations on the crystals (Fig. 9), no conclusions in regard to the system to which they belonged could be drawn from the measurements of the angles. The cleavage of the salt is basal and well marked.

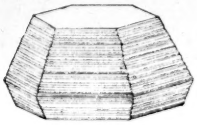


FIG. 9.

Mr. C. P. Brigham, working in this laboratory, has obtained a double salt of bismuth and rubidium chlorides, which, as he has shown, corresponds in formula to the salt above described.[1]

On adding a considerable excess of antimony chloride to a solution of the complex salt discussed above, and evaporating, crystals of an entirely different form are obtained. These were not investigated crystallographically, but may be described as compact crystals, sometimes resembling a rhombohedron in general shape. They are pale yellow in color. This is noteworthy, because the more complex salt (described above) and the simpler one (discussed below) are both colorless. It is to be remembered, however, that the salt $Cs_2Sb_5Cl_9$ is also yellow. As the formula

[1] See the following article.

of this rubidium salt is not very simple, and as the substance could not be recrystallised, on account of the strong tendency towards the formation of the very complex salt, the formula suggested below can hardly be considered as definitely established. The analytical results obtained from different samples varied considerably, and it does not appear possible to obtain the salt in pure condition.

One sample gave the following results:

0.3382 gram gave 0.1348 gram Sb_2S_3 (28.45 per cent. Sb), and 0.1560 gram RbCl (32.60 per cent. Rb).

0.2712 gram gave 0.4217 gram AgCl (38.45 per cent. Cl).

In another sample 0.1530 gram gave 0.2392 gram AgCl (38.66 per cent. Cl).

	Calculated for $3SbCl_3.5RbCl$.		Found.
3Sb	358.8	28.03	28.45
5Rb	426.0	33.28	32.60
14Cl	495.18	38.69	38.45 and 38.66
	1279.98	100.00	99.50

In view of the fact that this salt is formed only in presence of an excess of antimony chloride, the above results may be considered as almost conclusive evidence in favor of the formula $Rb_5Sb_8Cl_{14}$. This salt is stable in comparatively dry air.

If the excess of antimony chloride added in the experiment last described be *very* great, a colorless salt crystallising in elongated, apparently orthorhombic, crystals is obtained, instead of the yellow salt. These crystals have brilliant faces when fresh, but on exposure to the air under ordinary conditions they soon become covered with an opaque white deposit, which probably consists of oxychloride of antimony, formed by surface decomposition of the salt. The compound was found to have a very simple formula, though the presence of so large an excess of antimony chloride at the time of its formation naturally makes the analytical results somewhat unsatisfactory. The salt cannot, of course, be recrystallised. As in the case of the salt just described, it was prepared for analysis merely by drying between filtering paper and then in a desiccator over calcium chloride.

0.4343 gram gave 0.2133 gram Sb_2S_3 (35.05 per cent. Sb), and 0.1489 gram RbCl (24.23 per cent. Rb).

0.4563 gram gave 0.2242 gram Sb_2S_3 (35.07 per cent. Sb), and 0.7495 gram AgCl (40.62 per cent. Cl).

	Calculated for $RbSbCl_4$.		Found.
Rb	85.2	24.60	24.23
Sb	119.6	34.54	35.05 and 35.07
4Cl	141.48	40.86	40.62
	346.28	100.00	99.90

The formula of this salt is therefore $RbSbCl_4$.

Summary.

The following is a list of the compounds of antimony chloride, with the chlorides of rubidium and cæsium obtained in this investigation. The formula of the first of the rubidium salts must be considered as somewhat doubtful.

$Cs_3Sb_2Cl_9$

$Rb_{22}Sb_{10}Cl_{58}$
$Rb_5Sb_3Cl_{14}$
$RbSbCl_4$

These formulas show that the elements in question have a marked tendency towards the formation of complex double chlorides. The most important conclusion, however, to be drawn from the present investigation is that neither the salt described by Godeffroy as $SbCl_3.6CsCl$ nor that described as $SbCl_3.6RbCl$ corresponds in composition to the formula proposed by him.

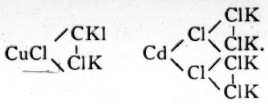
Theoretical.

There are now two well-established exceptions to the general law in regard to the composition of the double chlorides, namely, the salts $CuCl_2.2KCl$[1] and $CdCl_2.4KCl$[2]. It is to be noticed, however, that the structure of the salt $Rb_{22}Sb_{10}Cl_{58}$ cannot be represented on the same general system as that of the ordinary double chlorides, where two chlorine atoms are supposed to be analogous in function to one oxygen atom in the oxygen salts. This statement holds true even if the formula of this chloride be somewhat simpler than that here proposed. Hence this compound is perhaps quite as exceptional as the two simpler salts mentioned. In view of these facts the author offers the following formulas as suggestions of the possible structure of these compounds. Some of the bonds indicated are perhaps unnecessary. They are

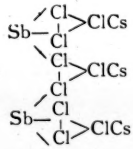
[1] Mitscherlich: Ann. chim. phys. [2] **73**, 384.

[2] C. v. Hauer: Wien. Akad. Ber. **15**, 23. These results have recently been confirmed by Dr. G. M. Richardson.

inserted merely for the sake of representing the chlorine atoms as invariably trivalent. The essential point is the conception that a group of three chlorine atoms can have three free valencies.



According to this method of writing, the salt $Cs_3Sb_2Cl_9$ could be represented by a symmetrical formula,



By doubling the formula it could, however, be written symmetrically according to the usual method, representing the chlorine atoms as always in pairs. By a combination of the two ideas—that a pair of chlorine atoms can have two free valencies, and that a group of three can have three free valencies—we can write a symmetrical formula for the salt $Rb_{23}Sb_{10}Cl_{53}$. It seems needless to give this structural formula here, as it covers a very large space. The formula of the salt $Rb_3Sb_3Cl_{14}$ can be written by representing all the chlorine atoms as united in pairs. As this is perhaps the simplest conception, an unnecessary departure from it would hardly be justifiable.

V.—On Some Double Halides of Bismuth.[1]

By C. Pliny Brigham.

Double halides of bismuth and potassium have been described as follows:

$BiCl_3.3KCl$, Arppe } Spec. Acad. d. 9 Oct. 1844, and Berzelius'
$BiCl_3.2KCl$, Arppe } Jahrsb. **25**, 279.
$BiCl_3.2KCl + 2H_2O$, Jacquelaine: Ann. chim. phys. **66**, 113.

[1] From the author's thesis, presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University, June, 1891.

$BiI_3.2KI + H_2O$, Arppe } Spec. Acad. 5 Juni, 1844, and Ber-
$BiI_3.4KI + HI$ (?), Arppe } zelius' Jahrsb. **25**, 284.
$BiCl_3.2KBr + 1\frac{1}{2}H_2O$, Atkinson: J. Chem. Soc. 1883, 292.

Of these I have worked only with the chlorides.

There are recorded a number of other double halides of bismuth which are here tabulated.

$BiCl_3.2NaCl + 3H_2O$, Jacquelaine: } Ann. chim. phys. **66**, 113.
$BiCl_3.NH_4Cl$, Jacquelaine: }

$BiCl_3.2NH_4Cl$, Deherain: } Compt. rend. **54**, 724.
$BiCl_3.3NH_4Cl$, Deherain: }

$BiBr_3.3NH_4Cl + H_2O$, Muir: } J. Chem. Soc. 1876, 148.
$BiBr_3.2NH_4Cl + 3H_2O$, Muir: }

$BiBr_3.2NH_4Cl + 5H_2O$, Nicklès: J. Chem. Soc. 1876, 148.

$2BiBr_3.5NH_4Cl + H_2O$, Muir: J. Chem. Soc. 1877, 28.

Of other double salts of bismuth there are two of the composition:

$3K_2SO_4.Bi_2(SO_4)_3$, } Berzelius' Jahrsb. **25**, 286.
$2K_2SO_4.BiO(SO_4)_2$, }

I speak of these simply because in a method of analysis employed for the determination of chlorine in the double chloride $BiCl_3.2KCl + 2H_2O$, I obtained a salt, a double sulphate, differing in composition from either of the above, and mention of which I have been unable to find in the literature.

Godeffroy[1] describes the salts $BiCl_3.6RbCl$ and $BiCl_3.6CsCl$, which are plainly marked exceptions to Professor Remsen's law. With these facts at hand, the following work on the double salts of bismuth chloride with the chlorides of rubidium and cæsium was undertaken to determine whether or not these compounds really exist.

Method of Analysis.

Although Godeffroy in his article gives the results of complete analyses of the different salts described therein, he fails to give the method employed, which would indicate, to say the least, that they are simple; but the analysis of the double chlorides of bismuth and the alkalies presents many difficulties, a few of which I will mention. Freshly prepared ammonium sulphide was added to the double salt in water; the sulphide of bismuth thus formed was filtered off on a washed filter, washed with water containing a little hydrogen sulphide, dried in an air-bath at 90°, scraped

[1] Berichte **8**, 9, und Zeitschrift des allgemeinen österreichischen Apotheker-Vereins.

into a weighed porcelain crucible, and, together with the ash from the filter, was treated with a few drops of pure concentrated nitric acid, the lid to the crucible being so placed as to avoid loss by spattering. The contents of the crucible were evaporated to dryness over a water-bath, heated to constant weight over a Bunsen burner, and finally over a blast-lamp, the bismuth oxide thus obtained melting without loss in weight. Before precipitating the chlorine in the filtrate from bismuth sulphide, it is first necessary to remove the excess of ammonium sulphide; to accomplish this, cadmium nitrate, free from arsenic, was added, and the cadmium sulphide formed filtered off. Copper sulphate was tried, but was found not to answer, as the sulphide of copper is partially soluble in ammonium sulphide. To the filtrate from cadmium sulphide was added a little nitric acid and silver nitrate, and the chlorine determined as silver chloride. The results obtained in this way were always 4 or 5 per cent. low; this error arises from the fact that when ammonium sulphide is used to precipitate the bismuth, some oxychloride comes down with the sulphide.

It was hoped that by dissolving the double salt in a little nitric acid and then adding a sulphide this trouble could be overcome, but if this is done a large amount of sulphur is thrown out with the bismuth sulphide, which seriously interferes with the determinations of bismuth.

After several months' work the following method was found to give satisfactory results.

A weighed portion of the salt, not more than 0.2 gram, is treated with about 20 cc. water containing 1 cc. pure concentrated hydrochloric acid, and heated nearly to boiling: there should be enough acid present to prevent the formation of any basic bismuth salts. Hydrogen sulphide is then passed in until the supernatant liquid becomes clear. The bismuth sulphide thus formed is filtered off on a quantitative filter, and washed with water containing a little hydrogen sulphide, dried, transferred to a weighed porcelain crucible, treated with a few drops of pure concentrated nitric acid, evaporated to dryness, and heated to a constant weight with a Bunsen burner, and finally over a blast-lamp. Bismuth is calculated from the oxide thus obtained.

Besides determining bismuth as the oxide, I also determined it directly from the sulphide by filtering this through a Gooch crucible and drying it at 100° to constant weight. Both of these methods give good results.

To determine the alkali, the filtrate is evaporated to dryness, dissolved again in a little water, filtered into a weighed platinum crucible, evaporated to dryness on a water-bath, and then heated for two hours at 235° in an air-bath, and when cool weighed; in the case of cæsium it was heated only to about 170°. The crucible is then heated for a few seconds only over a Bunsen burner to a dull red heat and again weighed; the loss here is generally less than 0.0004 gram. To make the results more accurate, the alkali thus determined as the chloride must be dissolved in a little hot water and filtered, the filter burned and weighed; thus any insoluble matter present, such as silicates, from the glass vessel used in evaporation can be detected and their weight subtracted from the weight of the alkali obtained. This method gives good results.

To determine chlorine a second sample of the salt is dissolved in about 30 cc. of water, containing several cubic centimeters of pure concentrated nitric acid, free from chlorine, and heated almost to boiling, when about 15 cc. more of nitric acid is added; this large excess of acid is necessary to prevent the formation of any basic bismuth salts; the chlorine is then precipitated by a not too weak solution of silver nitrate; the silver chloride is filtered off in a Gooch crucible, first washed with water containing nitric acid, and finally with water alone. The results for chlorine obtained in this way are entirely satisfactory.

Di-potassium Chloro-bismuthite,
$K_2BiCl_5 + 2H_2O$, ($BiCl_3.2KCl + 2H_2O$).

Arppe describes a salt K_3BiCl_6, ($BiCl_3.3KCl$), and states that when three molecular weights of bismuth oxide are dissolved in hydrochloric acid and two molecular weights of potassium chloride are added, on evaporation rhombic crystals separate out, which on analysis can be shown to have the composition K_2BiCl_5.

Following these directions closely I obtained beautiful four-sided crystals with two opposite angles cut off, thus presenting a six-sided appearance; the analysis of this salt showed it to have the composition $BiCl_3.2KCl + 2H_2O$.

The results obtained are here given:

0.1421 gram salt gave 0.0659 gram Bi_2O_3 = 0.0591 gram Bi.
0.1472 gram salt gave 0.2115 gram AgCl = 0.0523 gram Cl.
0.1419 gram salt gave 0.0417 gram KCl = 0.0219 gram K.
0.1025 gram salt lost 0.0074 gram H_2O.

	Calculated for $BiCl_3.2KCl + 2H_2O$.	Found.
Bi	41.63	41.57
K	15.66	15.49
Cl	35.48	35.51
H_2O	7.20	7.18

This salt is stable in the air; it does not lose its water of crystallisation in a desiccator, but when heated to 100° becomes anhydrous. It dissolves in moderately concentrated hydrochloric acid, and can be recrystallised from the same without any change in composition. Its crystallising power is very great.

All attempts to get the salt with three molecules of potassium chloride were fruitless. Bismuth oxide and potassium chloride were mixed in the exact proportions, one molecule of the former to six of the latter, yet the only salt obtained was $K_2BiCl_5 + 2H_2O$. Again a large excess of potassium chloride was used, and under these conditions potassium chloride crystallised out first and then the double salt with two molecules of the alkali chloride. Hence I feel justified in asserting that no salt of the formula K_2BiCl_6 exists.

Although no description of a double salt of bismuth and potassium chlorides containing less than two atoms of potassium to one of bismuth could be found, an investigation on this point was made, when a salt of the composition $KBiCl_4 + H_2O$, $(BiCl_3.KCl + H_2O)$ was obtained.

Mono-potassium Chloro-bismuthite,
$KBiCl_4 + H_2O$, $(BiCl_3.KCl + H_2O)$.

When bismuth oxide and potassium chloride are dissolved in hydrochloric acid in the proportion of 2½ molecules of the former to 2 of the latter, and the solution evaporated to a syrupy consistency, beautiful fiber-like needles radiating from centres crystallise out. If the solution be not sufficiently concentrated by evaporation, the salt $K_2BiCl_5 + 2H_2O$ invariably crystallises out. The analysis of this salt, dried first by means of a porous plate and then between filter-papers, gave these results:

I. 0.4109 gram salt gave 0.2338 gram Bi_2O_3 = 0.2096 gram Bi.
II. 0.1758 gram salt gave 0.1005 gram Bi_2O_3 = 0.0901 gram Bi.
III. 0.1910 gram salt gave 0.1095 gram Bi_2O_3 = 0.0982 gram Bi.

I. 0.1910 gram salt gave 0.0363 gram KCl = 0.0190 gram K.
II. 0.1753 gram salt gave 0.0324 gram KCl = 0.017 gram K.

I. 0.1752 gram salt gave 0.2503 gram AgCl = 0.0619 gram Cl.
II. 0.2082 gram salt gave 0.2976 gram AgCl = 0.0736 gram Cl.
I. 0.4109 gram salt lost 0.019 gram H_2O.
II. 0.45405 gram salt lost 0.0167 gram H_2O.

	Calculated for $BiCl_3.KCl + H_2O$.	Found. I.	II.	III.
Bi	51.11	51.01	51.25	51.39
K	9.62	9.96	9.66	...
Cl	34.85	35.31	35.32	...
H_2O	4.43	4.52	...	3.67

The sample of salt used in analysis III was made from a solution containing a very large excess of bismuth chloride, which readily accounts for the high percentage of bismuth and the low percentage of water found. This salt is stable in the air; it cannot be recrystallised except from a strong solution of bismuth chloride, from which the salt cannot be completely freed. When crystallised from hydrochloric acid it goes over into $K_2BiCl_5 + 2H_2O$, which appears to be the most stable of the double chlorides of bismuth and potassium. This salt, $KBiCl_4 + H_2O$, when placed in a desiccator over chloride of calcium, loses one-half of its water, while the remainder cannot be driven off below 100°.

Weight of the tube + salt (dried on a porous plate),	8.8701 grams.
" " " empty,	8.4592
" " salt,	0.4109
" " tube + salt dried to constant weight in a desiccator,	8.8608
" " tube + salt heated to constant weight at 105°,	8.8515
Loss in weight of salt dried at 105°,	0.0186
" " " " in a desiccator,	0.0093
Percentage of water lost by drying in a desiccator,	2.26
Total percentage of water lost when the salt is heated to constant weight at 105°,	4.52

Thus it appears that in the salt dried over calcium chloride, there is ½ a molecule of water of crystallisation.

A sample of this salt was heated to 140°, but the loss in weight indicated the presence of but 1 molecule of water. When a higher temperature was tried the salt underwent a slight decomposition.

Potassium-bismuth Alum, $KBi(SO_4)_2$, $[K_2SO_4.Bi_2(SO_4)_3]$.

In trying to overcome the difficulties of analysing the double chloride for chlorine, a method was tried which unexpectedly yielded a salt of the composition $KBi(SO_4)_2$.

A weighed quantity of the double chloride of bismuth and potassium was placed in an Erlenmeyer flask and treated with concentrated sulphuric acid, the hydrochloric acid set free being conducted into a dilute solution of sodium hydroxide. After heating the contents of the flask for several hours, fine needle-shaped crystals appeared on cooling. On the addition of water they dissolved, and by evaporation of the solution they were again deposited in the needle form, as well as in beautiful glistening plates.

The analysis of these crystals shows them to have the composition $K_2SO_4.Bi_2(SO_4)_3$, or $KBi(SO_4)_2$, analogous to ordinary alum, $KAl(SO_4)_2 + 12H_2O$. As might be expected, this salt has no water of crystallisation, being formed in concentrated sulphuric acid. These are the results obtained:

I. 0.3478 gram salt gave 0.1841 gram Bi_2O_3 = 0.1650 gram Bi.
II. 0.2081 gram salt gave 0.1109 gram Bi_2O_3 = 0.0994 gram Bi.
I. 0.2081 gram salt gave 0.0416 gram K_2SO_4 = 0.0187 gram K.
II. 0.2388 gram salt gave 0.0477 gram K_2SO_4 = 0.0215 gram K.
I. 0.3478 gram salt gave 0.3672 gram $BaSO_4$ = 0.1511 gram SO_4.
II. 0.1248 gram salt gave 0.1337 gram $BaSO_4$ = 0.0550 gram SO_4.

	Calculated for $KBi(SO_4)_2$.	Found. I.	Found. II.
Bi	47.36	47.44	47.77
K	8.91	8.99	8.98
SO_4	43.72	43.46	44.10

The method of analysis is as follows: Dissolve a weighed quantity of the salt in water and hydrochloric acid, add barium chloride to precipitate all the sulphuric acid as barium sulphate: there must be enough hydrochloric acid present to prevent the formation of any basic bismuth salts. Filter off into a Gooch crucible the barium sulphate, wash first with dilute hydrochloric acid, and finally with water; dry and weigh.

The bismuth in the filtrate can be determined, if too much acid be not present; or a new sample dissolved in hydrochloric acid and water may be taken: in this case the determination is exactly the same as in the case of the double chlorides.

To determine the potassium, a third sample is dissolved as before, hydrogen sulphide passed in to precipitate the bismuth, which is filtered off, and the filtrate evaporated to dryness, redissolved, filtered into a weighed platinum dish and again evaporated to dryness. 3 to 5 drops of sulphuric acid is then added and the substance heated to constant weight over a free flame, the acid salt first formed being transformed finally into potassium sulphate, from the weight of which the potassium is calculated.

This salt possesses the remarkable property of being quite insoluble in cold water; on boiling, however, it is decomposed into a bismuthyl sulphate of the composition $(BiO)_2SO_4 + 2H_2O$.

A quantity of the salt $KBi(SO_4)_2$ was boiled in water and the insoluble part filtered off and dried on a porous plate, and analysed with the following results:

0.0896 gram salt gave 0.0717 gram $Bi_2O_3 = 0.0643$ gram Bi.
0.0896 gram salt gave 0.0357 gram $BaSO_4 = 0.0147$ gram SO_4.

	Calculated for $(BiO)_2SO_4 + 2H_2O$.	Found.
Bi	71.72	71.74
SO_4	16.55	16.39

In the filtrate potassium and sulphuric acid were found, hence the decomposition may be expressed thus:

$$2BiK(SO_4)_2 + 2H_2O = (BiO)_2SO_4 + K_2SO_4 + 2H_2SO_4,$$
$$\text{or} = (BiO)_2SO_4 + 2KHSO_4 + H_2SO_4.$$

Potassium-antimony Alum.

By analogous methods of work I hoped to obtain a double sulphate of antimony and potassium, as well as one of arsenic and potassium, thus making more complete a series of double salts analogous to the well-known alums.

I first made the double chloride of antimony and potassium, then boiled it with concentrated sulphuric acid for eight hours: on cooling, well crystallised needles separated out. On the addition of water, instead of behaving like the corresponding bismuth compound, it immediately broke down into basic antimony sulphate. A second sample of the double chloride was heated for two days with concentrated sulphuric acid: on cooling the same crystalline mass appeared, and on the addition of water acted as before. A third sample was heated for eight hours with concentrated sulphuric acid, and instead of trying to recrystallise the mass, the excess of acid was poured off and the salt placed on a porous

plate to dry: by this treatment the salt absorbed moisture from the air, and changed gradually into basic antimony sulphate. It was next placed in a vacuum over soda-lime and caustic potash. At the end of one month it was fairly dry, although the excess of acid had not entirely disappeared. An analysis was made which gave 17.9 per cent. antimony and 0.78 per cent. potassium, or a ratio between the atoms of antimony and potassium of 0.489 to 0.0669, instead of 1 to 1.

Further investigation of this salt was given up, as it was found impossible to get it pure enough for sharp analysis. The work done tends, however, to show the non-existence of a salt of the composition $KSb(SO_4)_2$ analogous to $KBi(SO_4)_2$. This is not surprising, since antimony is a much weaker base than bismuth and has greater acid properties; hence we can trace a gradation: in ordinary alum, $KAl(SO_4)_2$, we have great stability, especially toward water; with bismuth-potassium sulphate, we find a tendency to break down on boiling with water, while in the case of antimony no double salt, $KSb(SO_4)_2$, can be obtained. Arsenic having still greater acid properties will probably act like antimony and show no signs of forming a double sulphate. It would be interesting to see whether an analogous compound containing boron could be made.

Tri-rubidium Chloro-bismuthite, Rb_3BiCl_6, ($BiCl_3.3RbCl$).

The only work on the double chlorides of bismuth and rubidium was done by Godeffroy, who published his results in 1875. He describes and gives a complete analysis of the salt Rb_6BiCl_9, ($BiCl_3.6RbCl$), which forms a marked exception to the law regarding the composition of the double halides. As many of the salts described by Godeffroy which have appeared as exceptions to the law, have by subsequent work been shown not to exist, it was deemed advisable carefully to investigate this double chloride, and determine first whether or not it has the composition Rb_6BiCl_9; secondly, whether by the further addition of bismuth or rubidium chloride a salt can be formed containing a greater or less percentage of bismuth similar to the salts obtained in the case of potassium. His description of the salt is briefly this:

By evaporation of a hydrochloric acid solution of bismuth chloride with rubidium chloride, beautiful crystals separate out. His analysis is as follows:

0.1535 gram salt gave 0.191 gram AgCl = 0.0473 gram Cl.
0.1535 gram salt gave 0.036 gram Bi_2O_3 = 0.03088[1] gram Bi.
0.423 gram salt gave 0.707 gram Rb_2PtCl_6 = 0.2077 gram Rb.

	Calculated for $BiCl_3.6RbCl$.	Found.
Bi	20.00	20.120
Cl	30.72	30.803
Rb	49.28	49.110

In order to give the best chance for the formation of this salt, rubidium chloride was dissolved in a little cold dilute hydrochloric acid, and drop by drop to this was added a hydrochloric acid solution of bismuth chloride, as the presence of a large excess of rubidium chloride should give the most favorable opportunity for the formation of a salt containing six atoms of rubidium, if formed at all. On the addition of the slightest quantity of bismuth chloride a voluminous crystalline precipitate was immediately formed, no evaporation being necessary. Godeffroy states that there is no precipitate formed when solutions of bismuth and rubidium chlorides are mixed. A small quantity of this precipitate was removed, dried on a porous plate, and analysed with the following results:

0.1884 gram salt gave 0.0644 gram Bi_2O_3 = 0.0577 gram Bi.
0.1427 gram salt gave 0.0761 gram RbCl = 0.0538 gram Rb.
0.1999 gram salt gave 0.2551 gram AgCl = 0.0631 gram Cl.

	Calculated for $BiCl_3.3RbCl$.	Found.
Bi	30.72	30.65
Rb	37.84	37.68
Cl	31.42	31.54

On heating a sample of this salt for two hours at 110° it lost in weight but slightly, giving only 0 2 per cent. loss, which was probably due to incomplete drying. Thus the analysis of this precipitate shows that it has the composition Rb_3BiCl_6, ($BiCl_3$. 3RbCl), and not Rb_6BiCl_9, ($BiCl_3.6RbCl$).

Another portion of the precipitate was dissolved in moderately concentrated hydrochloric acid and the solution evaporated, when beautiful transparent crystals separate out, which, on the addition of concentrated hydrochloric acid, become opaque. These crystals are diamond-shaped, very regular in form, and similar to those of the potassium salt $K_2BiCl_5 + 2H_2O$, but without the truncations of the two opposite angles. The crystallising power of this salt is weak, consequently the crystals are of small size, but

[1] A miscalculation; should be 0.032274 gram Bi.

quite uniform. These crystals were dried on porous plates and then pressed between drying paper, and on analysis gave the following results:

I. 0.1552 gram salt gave 0.0536 gram Bi_2O_3 = 0.0480 gram Bi.
II. 0.2132 gram salt gave 0.0734 gram Bi_2O_3 = 0.0658 gram Bi.
I. 0.1835 gram salt gave 0.0985 gram RbCl = 0.0696 gram Rb.
II. 0.1609 gram salt gave 0.0860 gram RbCl = 0.0608 gram Rb.
I. 0.1349 gram salt gave 0.1777 gram AgCl = 0.0439 gram Cl.
II. 0.2093 gram salt gave 0.2670 gram AgCl = 0.0660 gram Cl.

	Calculated for $BiCl_3.3RbCl$.	Found. I.	II.
Bi	30.72	30.97	30.86
Rb	37.84	37.93	37.76
Cl	31.42	31.49	31.53

The recrystallised precipitate, when heated to 110° for two hours, lost but slightly in weight, showing that there is no water of crystallisation in the salt, the decrease being due to insufficient drying, a little hydrochloric acid probably being present.

This salt dissolves without decomposition in dilute hydrochloric acid, and, on evaporation of the solution, it always crystallises out in the same form. Water decomposes it with the formation of basic bismuth chloride and rubidium chloride.

Other attempts to obtain the salt of Godeffroy were made by using a cold concentrated solution of rubidium chloride and a cold dilute solution of bismuth chloride. Hot solutions also were used, but without success, the salt crystallising out always having the composition Rb_2BiCl_6.

A more complex Chloride of Rubidium and Bismuth,
$Rb_{23}Bi_{10}Cl_{53}$, ($10BiCl_3.23RbCl$) (?).

When bismuth oxide and rubidium chloride are mixed in the proportion of one molecular weight of the former to two of the latter, and the mixture dissolved in dilute hydrochloric acid and the solution evaporated, there separates out a salt crystallising in most varied forms resembling shapes of snow crystals, which, however, on standing, change and assume the form of hexagonal plates. These crystals are transparent, quite small, but very regular in habit. This salt was obtained in such small quantities that purification by crystallisation was impossible; in fact, when crystallised from hydrochloric acid it passes over into the compound Rb_2BiCl_6:

it can, however, be recrystallised from a solution of bismuth chloride.

The analysis of this salt did not give results sharp enough to lead to a definite formula. This is no doubt due to the impossibility of purifying it by repeated crystallisation. The following results were obtained:

I. 0.1563 gram salt gave 0.0603 gram Bi_2O_3=0.0541 gram Bi.
II. 0.2483 gram salt gave 0.0973 gram Bi_2O_3=0.0872 gram Bi.
I. 0.1563 gram salt gave 0.0719 gram RbCl=0.0508 gram Rb.
II. 0.2483 gram salt gave 0.1138 gram RbCl=0.0815 gram Rb.
I. 0.1525 gram salt gave 0.1956 gram AgCl=0 0484 gram Cl.
II. 0.1992 gram salt gave 0.2551 gram AgCl=0.0631 gram Cl.

	Calculated for $10BiCl_3.23RbCl$.	Found. I.	Found. II.
Bi	35.11	34.58	35.17
Rb	33.17	32.50	32.83
Cl	31.72	31.74	31.66

From analysis I. the calculated ratio between the bismuth and rubidium atoms is 1 : 2.296, and from analysis II., 1 : 2.275, and the formula which would seem most probable in view of these results is $Rb_{23}Bi_{10}Cl_{53}$, or $10BiCl_3.23RbCl$.

Were it not for certain facts established by Mr. C. E. Saunders[1] the above formula would seem highly improbable. This gentleman, working on the double chlorides of antimony and rubidium, obtained a salt crystallising in the same form, the analysis of which gave a ratio between the antimony and rubidium atoms of 1 : 2.296.

Bismuth being so closely related to antimony, and the work on the double chloride of the latter with rubidium having shown the existence of a salt of the probable composition $10SbCl_3.23RbCl$, it is not surprising that a similar compound of bismuth should be formed. From the results actually obtained by me in the analysis of the salt above described, I think it highly probable that the composition of this salt corresponds to the formula $Rb_{23}Bi_{10}Cl_{53}$.

The salt $Rb_{23}Bi_{10}Cl_{53}$ dissolves to a clear solution in dilute hydrochloric acid, from which on partial evaporation there crystallises out the salt Rb_3BiCl_6, which is the form that these elements always assume under ordinary conditions. In water this salt decomposes with the formation of basic bismuth chloride.

[1] See preceding article, p. 160.

Mono-rubidium Chloro-bismuthite,
$RbBiCl_4 + H_2O$, ($BiCl_3.RbCl + H_2O$).

Besides the compounds Rb_2BiCl_6 ($BiCl_3.3RbCl$), and $Rb_{23}Bi_{10}Cl_{53}$ ($10BiCl_3.23RbCl$), another was obtained which in all probability corresponds to the mono-potassium chloro-bismuthite of the composition $RbBiCl_4 + H_2O$.

It was found that, when 2½ molecular weights of bismuth oxide were dissolved in concentrated hydrochloric acid, and 2 molecular weights of rubidium chloride were added and the solution evaporated to a syrupy consistency, after a time white hair-like crystals formed, and finally the contents of the vessel became almost solid. The beaker in which the salt was formed was turned on its side and the liquid allowed to drain off, after which the crystals were transferred to a porous plate and finally dried between filter-papers. If the evaporation of the solution be stopped before the liquid becomes sufficiently concentrated for the formation of these needle-like crystals, crystals of the compound $10BiCl_3.23RbCl$ always separate out, while, on the contrary, should the evaporation be carried beyond the point at which the hair-like crystals first form, these needles, although they are formed, do not appear separate, but seem to start from points and form themselves into a solid mass radiating from these points as centres.

The rubidium chloride used in this experiment was found on analysis to be slightly impure, containing probably a slight trace of cæsium.

0.2522 gram RbCl gave 0.2866 gram $AgCl = 0.0708$ gram $Cl = 28.09$ per cent. Theoretical per cent. of chlorine in $RbCl = 29.34$.

The conditions under which this double salt is formed, in a very concentrated solution of bismuth chloride, give little opportunity for the purification of the salts used. Were this salt formed in dilute acid solution, any impurity present in the rubidium chloride might be removed by the difference in solubility of the double salts produced; but being formed in such concentrated solutions, where bismuth chloride is present in such large excess, and where it appears as if all of both constituents present enter into combination, it is not surprising that, if cæsium is the impurity in the rubidium chloride, it would be carried along by both constituents and enter into combination.

This is probably the reason why the analyses of the salt do not correspond to any simple formula, although the similarity in the method of formation and in appearance to the potassium salt of the composition $KBiCl_4 + H_2O$ makes it appear probable that it has the composition $RbBiCl_4 + H_2O$.

The results of the analyses of three different samples are as follows:

Sample A.

I. 0.1275 gram salt gave 0.0622 gram Bi_2O_3 = 0.0558 gram Bi.
II. 0.1223 gram salt gave 0.0598 gram Bi_2O_3 = 0.0536 gram Bi.

Sample B.

I. 0.1315 gram salt gave 0.0743 gram Bi_2S_3 = 0.0603 gram Bi.
II. 0.1263 gram salt gave 0.0643 gram Bi_2O_3 = 0.0576 gram Bi.
III. 0.4108 gram salt gave 0.2315 gram Bi_2S_3 = 0.1880 gram Bi.

Sample C.

I. 0.2150 gram salt gave 0.1212 gram Bi_2S_3 = 0.0984 gram Bi.
II. 0.1666 gram salt gave 0.0940 gram Bi_2S_3 = 0.0763 gram Bi.

Sample A.

I. 0.1275 gram salt gave 0.0394 gram RbCl = 0.0278 gram Rb.
II. 0.1223 gram salt gave 0.0379 gram RbCl = 0.0268 gram Rb.

Sample B.

I. 0.1315 gram salt gave 0.0408 gram RbCl = 0.0288 gram Rb.
II. 0.1263 gram salt gave 0.0408 gram RbCl = 0.0288 gram Rb.

Sample C.

II. 0.1666 gram salt gave 0.0520 gram RbCl = 0.0368 gram Rb.

Sample A.

I. 0.1204 gram salt gave 0.1564 gram AgCl = 0.0387 gram Cl.
II. 0.1829 gram salt gave 0.2379 gram AgCl = 0.0588 gram Cl.

Sample B.

I. 0.1203 gram salt gave 0.1562 gram AgCl = 0.0386 gram Cl.
II. 0.1739 gram salt gave 0.2261 gram AgCl = 0.0559 gram Cl.

Sample C.

I. 0.2189 gram salt gave 0.2848 gram AgCl = 0.0704 gram Cl.
II. 0.2578 gram salt gave 0.3350 gram AgCl = 0.0828 gram Cl.

Sample A.

I. 0.4347 gram salt lost 0.011 gram H_2O, heated for 2 hours at 105°.

Sample B.

I. 0.4151 gram salt lost 0.0043 gram H_2O, heated for 2 hours at 105°.

Sample C.

I. 0.4085 gram salt lost 0.0067 gram H_2O, heated for 2 hours at 105°.

II. 0.1957 gram salt lost 0.00295 gram H_2O, heated for 2 hours at 105°.

Sample A.

	Calculated for $RbBiCl_4 + H_2O$.	Calculated for $RbBiCl_4$.	Found. I.	Found. II.
Bi	45.89	47.77	43.73	43.83
Rb	18.84	19.62	21.83	21.89
Cl	31.29	32.58	32.10	32.17
H_2O	3.97	...	2.53	...

Sample B.

	Calculated for $RbBiCl_4 + H_2O$.	Calculated for $RbBiCl_4$.	Found. I.	Found. II.	Found. III.
Bi	45.89	47.77	45.89	45.64	45.77
Rb	18.84	19.62	21.29	22.54	...
Cl	31.29	32.58	32.09	32.14	...
H_2O	3.97	...	1.03	...	...

Sample C.

	Calculated for $RbBiCl_4 + H_2O$.	Calculated for $RbBiCl_4$.	Found. I.	Found. II.
Bi	45.89	47.77	45.78	45.82
Rb	18.84	19.62	...	22.11
Cl	31.29	32.58	32.16	32.11
H_2O	3.97	...	1.64	1.50

The bismuth in analyses I. and III., sample *B*, and I. and II., sample *C*, was determined as the sulphide, while that in I. and II., sample *A*, and II., sample *B*, was calculated from the oxide.

It will be seen on comparing the results calculated for $RbBiCl_4 + H_2O$ with the percentages found, that while there is a discrepancy in the case of rubidium and water, the percentages for bismuth and chlorine are close.

This salt is decomposed by water, but yields a clear solution when treated with dilute hydrochloric acid, from which on slight evaporation the salt $BiCl_3.3RbCl$ separates.

All efforts to obtain salts composed of bismuth and rubidium

chlorides other than have here been described have proved fruitless. From these facts it appears to follow that the salt $BiCl_3.6RbCl$, described by Godeffroy, does not exist.

Cæsium-bismuth Chlorides.

As with rubidium, so with cæsium, Godeffroy describes a salt of the composition $BiCl_3.6CsCl$, and to determine whether such a compound exists the following work was undertaken. On analysis the cæsium chloride obtained from one of the best known dealers was found to be very impure, containing most probably rubidium and potassium. Before beginning the investigation of the double chloride it was therefore necessary to purify this salt. The method[1] employed depends on the difference in solubility of the double salts of antimony-rubidium chloride and antimony-cæsium chloride, the former being soluble in concentrated hydrochloric acid, the latter not.

The cæsium chloride was dissolved in moderately concentrated hydrochloric acid, and a solution of antimony chloride in hydrochloric acid added, until it ceased to give a precipitate. The solution was allowed to stand until clear, when the supernatant liquid was poured off. Concentrated hydrochloric acid was added to the precipitate, in which case any rubidium-antimony chloride present would dissolve. This liquid was poured off when the precipitate remaining should contain only cæsium-antimony chloride. This was dissolved in hot concentrated hydrochloric acid, and hydrogen sulphide passed in for a *long* time, as the large quantity of acid used to dissolve the salt prevents the complete precipitation of the antimony at once. The antimony sulphide was filtered off, and the filtrate containing the cæsium chloride was evaporated to dryness in a *platinum* dish; if a glass or porcelain vessel is used, some alkali from the glass will be dissolved; to drive off the last trace of hydrochloric acid, it was heated to 130° in an air-bath.

The cæsium chloride thus treated was found to be much purer than that with which I started; yet a second purification seemed advisable, the result of which gave me a small quantity of the salt, which on analysis gave these results:

0.1711 gram CsCl gave 0.147 gram $AgCl = 0.0363$ gram Cl $= 21.23$ per cent. Theoretical percentage of chlorine in cæsium chloride $= 21.05$.

[1] Ann. Chem. (Liebig) **181**, 183.

This is probably as pure as cæsium chloride can be obtained by this method; the quantity of the salt would not permit a third purification.

Godeffroy[1] in his description of the salt $BiCl_3.6CsCl$ says that, by mixing solutions of bismuth and cæsium chlorides in hydrochloric acid, he obtained a precipitate which is difficultly soluble, and gave these results:

0.900 gram salt gave 0.861 gram AgCl = 0.213 gram Cl.
0.900 gram salt gave 0.154 gram Bi_2O_3 = 0.138 gram Bi.
0.515 gram salt gave 0.788 gram Cs_2PtCl_6 = 0.3095 gram Cs.

	Calculated for $BiCl_3.6CsCl$.	Found.
Cl	24.10	23.67
Bi	15.68	15.37
Cs	60.22	60.09

Following these directions, to a saturated solution of cæsium chloride in dilute hydrochloric acid a solution of bismuth chloride was added drop by drop, when a voluminous precipitate, difficultly soluble, was formed. A close examination of this precipitate showed the presence of two distinct kinds of crystals. However, to follow Godeffroy's direction and obtain his salt this precipitate as obtained was analysed. A sample dried on a porous plate and finally between filter-papers gave these results:

I. 0.171 gram salt gave 0.0701 gram Bi_2S_3 = 0.0569 gram Bi.
II. 0.1881 gram salt gave 0.0782 gram Bi_2S_3 = 0.0635 gram Bi.
I. 0.171 gram salt gave 0.0862 gram CsCl = 0.0681 gram Cs.
II. 0.1881 gram salt gave 0.0947 gram CsCl = 0.0748 gram Cs.
I. 0.1534 gram salt gave 0.1693 gram AgCl = 0.0418 gram Cl.
II. 0.1507 gram salt gave 0.1671 gram AgCl = 0.0413 gram Cl.

	Calculated for $BiCl_3.2CsCl$.	Calculated for $BiCl_3.6CsCl$.	Found. I.	Found. II.
Bi	31.93	15.68	33.29	33.76
Cs	40.84	60.22	39.79	39.74
Cl	27.22	24.10	27.28	27.41

These results show that the precipitate is most probably a mixture, as it corresponds to no simple salt, but has a composition somewhat near $BiCl_3.2CsCl$.

The precipitate dissolves easily in warm dilute hydrochloric acid, one of the constituents apparently with more ease than the other, so that it is quite an easy matter to separate and obtain

[1] Zeitschrift des allgemeinen österreichischen Apotheker-Vereins.

them both in pure condition by recrystallisation. On evaporation of a solution of the precipitate in hydrochloric acid, the more compact-looking crystals which settled to the bottom of the precipitate formed yellowish, elongated pyramids; while the others, which are the more easily soluble, assume a flaky appearance. These are white and transparent.

After separation, each lot was recrystallised twice from dilute hydrochloric acid, and although but a small quantity of each was obtained, they appeared quite pure and gave excellent results on analysis.

Salt of the Composition $Cs_2Bi_2Cl_9$, ($2BiCl_3.3CsCl$).

That part of the precipitate formed by mixing solutions of cæsium and bismuth chlorides in hydrochloric acid, which on recrystallisation forms elongated pyramids, yellow in color, has the composition $Cs_2Bi_2Cl_9$, as shown by the following analytical results:—

0.1587 gram salt gave 0.072 gram Bi_2S_3 = 0.0585 gram Bi.
0.1587 gram salt gave 0.0708 gram CsCl = 0.0559 gram Cs.
0.1390 gram salt gave 0.1586 gram AgCl = 0.0392 gram Cl.

	Calculated for $2BiCl_3.3CsCl$.	Found.
Bi	36.68	36.84
Cs	35.18	35.22
Cl	28.13	28.20

This salt, on treatment with water, decomposes with the formation of oxychloride of bismuth and cæsium chloride; in cold dilute hydrochloric acid it is difficultly soluble, but dissolves rapidly when warmed. With the formation of this salt, the similarity between the elements bismuth and antimony is again shown, as the chloride of the latter with cæsium chloride only forms a salt of the composition $Cs_3Sb_2Cl_9$.

Tri-cæsium Chloro-bismuthite, Cs_3BiCl_6, ($BiCl_3.3CsCl$).

That part of the precipitate which crystallises in thin transparent plates has the composition Cs_3BiCl_6.

The results obtained on analysis of this salt are as follows:

I. 0.1189 gram salt gave 0.0376 gram Bi_2S_3 = 0.0305 gram Bi.
II. 0.1730 gram salt gave 0.0544 gram Bi_2S_3 = 0.0442 gram Bi.
II. 0.1730 gram salt gave 0.1063 gram CsCl = 0.0829 gram Cs.
I. 0.0817 gram salt gave 0.0860 gram AgCl = 0.0313 gram Cl.

	Calculated for $BiCl_3.3CsCl$.	Found. I.	II.
Bi	25.37	25.68	25.53
Cs	48.67	...	48.51
Cl	25.95	26.08	...

Through an accident the determination of cæsium in sample I. was lost.

The behavior of this salt is much like that of the composition $Cs_2Bi_2Cl_9$. It is difficultly soluble in cold dilute hydrochloric acid, but when warmed dissolves easily.

In the case of the double chlorides of rubidium and cæsium with bismuth, it was so difficult to obtain the compounds well crystallised that an investigation of their crystallographic properties was not undertaken.

Conclusion.

The principal results of this investigation are these:

I. Of the three double chloro-bismuthites of potassium only the one described by Jacquelaine, $(BiCl_3.2KCl + 2H_2O)$,[1] exists, while one of the composition $(BiCl_3.KCl + H_2O)$, not described in the literature, can be formed under certain conditions.

II. No salt of the composition Rb_6BiCl_9 exists, but from the chlorides of bismuth and rubidium the following salts can be formed: Rb_3BiCl_6, $Rb_{23}Bi_{10}Cl_{53}$, $RbBiCl_4 + H_2O$.

III. The salt to which Godeffroy ascribes the composition $BiCl_3.6CsCl$ is a mixture of the two salts Cs_3BiCl_6 $(BiCl_3.3CsCl)$ and $Cs_2Bi_2Cl_9$ $(2BiCl_3.3CsCl)$.

IV. As the atomic weight of the alkali in combination with bismuth increases, the amount of water of crystallisation decreases thus: $BiCl_3.2NaCl + 3H_2O$; $BiCl_3.2KCl + 2H_2O$; $BiCl_3RbCl + H_2O$; $BiCl_3.3CsCl$.

VI.—Experiments with Mercurous Hypochlorsulphite.

By J. E. Gilpin.

In connection with the work on the double halides that has been carried on in this laboratory for some time past, it was considered important to determine the molecular weight of one of these compounds by the aid of the specific gravity of its vapor. Capitaine[2] has described a compound of the formula $SCl_2.Hg_2Cl_2$ to which he gives the name mercurous hyposulphochloride (*chloride hyposulfureux*). According to the discoverer, this compound is volatile

[1] Ann. chim. phys. **66**, 113.

[2] J. prakt. Chem. **18**, 422.

without decomposition. It can be made in two ways: (1) either by subliming a mixture of mercuric chloride and sulphur, in which the product appears as a coating of fine yellow needles, which are removed from time to time as they are formed; or (2) by letting a mixture of mercurous chloride and sulphur chloride stand together in the dark for some time, and, after the excess of sulphur chloride has been distilled off, subliming the residue as in the first method.

In both cases the product has to be purified by sublimation. The product is crystalline, but cannot be recrystallised from solution, as solvents decompose it. During the investigation it was found that the substance does not act as Capitaine stated, but is decomposed. On resubliming the pure material partial decomposition took place, and when it was heated in a test-tube in a sulphuric-acid bath, decomposition began at about 80°, and if heated for some time to 180°, mercuric chloride was found coating the cool part of the tube while the sulphur remained at the bottom. The specimen made from mercuric chloride and sulphur and twice resublimed, gave on analysis:

0.4681 gram substance gave 0.0281 gram sulphur = 5.57 per cent. S.

0.4681 gram substance gave 0.3781 gram mercuric sulphide = 69.62 per cent. Hg.

0.4681 gram substance gave 0.4681 gram silver chloride = 24.72 per cent. Cl.

The calculated percentages for $SCl_2.Hg_2Cl_2$ are S = 5.58; Hg = 69.73; Cl = 24.68.

The specimen made from mercurous chloride and sulphur chloride gave the following results:

0.3893 gram substance gave 0.022 gram sulphur = 5.65 per cent. S.

0.3893 gram substance gave 0.3144 gram mercuric sulphide = 69.61 per cent. Hg.

0.3893 gram substance gave 0.3917 gram silver chloride = 24.87 per cent. Cl.

When this pure substance was sublimed again it was partly decomposed. Mercuric chloride remained at the bottom; but the upper part carefully removed gave the following analysis, showing that although it was partly decomposed, yet some of the original substance remained:

0.5113 gram substance gave 0.0258 gram sulphur = 5.04 per cent. S.

0.5113 gram substance gave 0.4135 gram mercuric sulphide = 69.71 Hg.

0.5113 gram substance gave 0.5086 gram silver chloride = 24.58 per cent. Cl.

After another sublimation of the last product the results showed that there was some free sulphur present, as the amounts were for sulphur 6.15 per cent., for mercury 68.55 per cent., and for chlorine 24.10 per cent.

This proof and the observations made when the substance is heated in a test-tube clearly establish the fact that decomposition takes place when it is heated to volatilise it.

The sulphur in the compound is in a very peculiar and sensitive condition. An attempt was made to add more chlorine to the compound in the hope of getting such a compound as $SCl_4.Hg_2Cl_2$; but it was found that when dry chlorine gas is passed over the substance at the ordinary temperature, all the sulphur is removed and passes off as sulphur chloride, leaving mercuric chloride behind in a perfectly pure state.

On account of the sensitive nature of the sulphur it was considered possible that this sulphur might act much more readily than free sulphur. Its action was tried on several amides, diphenyl-amine, aniline, and *p*-toluidine. Reactions took place easily in each case, but the mercuric chloride entered into the reaction, and compounds were formed whose true nature could not easily be determined. In the case of diphenyl-amine the reaction took place on heating to 80°; with aniline a reaction accompanied by a marked evolution of heat took place on stirring the substances together with a glass rod; and in the case of *p*-toluidine it was necessary to heat to 150°. The products were purified to remove any excess of the original substances, then dried and powdered. It was impossible to tell when the substances were pure; but the compound with *p*-toluidine was the easiest to purify on account of the solubility of the impurities. Diphenyl-amine gave a brown powder, aniline a blue one, and *p*-toluidine a black one. In each case the amides were treated with sulphur alone, and also with mercuric chloride, but the action did not take place unless both were present. The analyses showed the presence of sulphur, chlorine and mercury, and according to the results the compound is a mixture, or very complicated. The results agree nearly with a formula like $(C_6H_4.CH_3.NH_2)_2S_3Cl_3Hg_7$. Further experiments in this line will be undertaken as soon as possible.